VOL. XXX. AUGUST, 1903. NO. 2.

AMERICAN

CHEMICAL JOURNAL

CYANOGEN IODIDE AS AN INDICATOR FOR ACIDS.

BY J. H. KASTLE AND MARY E. CLARK.

It has been pointed out by E. von Meyer[1] that cyanogen iodide and hydriodic acid react to form hydrocyanic acid and iodine, thus:

$$HI + ICN = HCN + I_2.$$

This reaction seems to be a general one for iodides under proper conditions. We have found, for example, that cyanogen iodide also decomposes potassium iodide even in tolerably dilute solutions, and that it acts on mercuric iodide when the latter is suspended in water. It also liberates large amounts of iodine from ethyl iodide at 150° C. With the metallic iodides this reaction has been found to depend largely on the concentration. On normal solutions of potassium iodide, cyanogen iodide has been found to act at once in the cold with the liberation of iodine. This may be shown by

[1] J. prakt. Chem., 36, 292, 299.

bringing together 1 cc. of N-potassium iodide, 1 cc. of N/100 cyanogen iodide, and a small amount of starch paste. The solution becomes dark blue at once. On the other hand, if N/100 potassium iodide and N/100 cyanogen iodide be brought together in the presence of starch no iodide of starch is produced. If, however, to this colorless mixture a drop of acid be added, the solution becomes blue at once, indicating that cyanogen iodide acts upon hydriodic acid much more readily than it does upon potassium iodide. Indeed the reaction is one of extreme delicacy. It occurred to us, therefore, that it might not be without interest to determine the quantities of various acids required to effect the reaction in question. In order to do this, however, it was first necessary to test the conduct of cyanogen iodide towards potassium iodide at different concentrations. In all of our experiments a N/100 solution of cyanogen iodide in water was employed. The conduct of this solution towards potassium iodide was tested by bringing together 1 cc. N/100 cyanogen iodide, 1 cc. of potassium iodide of given concentration, and 1 cc. of a clear solution of starch containing 0.1 gram of starch in 100 cc. of water. The results of these observations are given in Table I. :

Table I.

Dilution of potassium iodide.	Color of the mixed solution.
N	Deep blue, immediately
N/2	" " "
N/8	" " not instantaneous
N/10	" " " "
N/20	Lighter blue, not "
N/50	Light blue, after standing some time
N/100	Colorless, even after standing some time

It has been found that small amounts of impurities greatly affect the results. Absolute cleanliness of apparatus is necessary in carrying out the tests if concordant results are to be obtained. The minutest trace of acids in the apparatus or reagents may often vitiate an entire series of experiments. It

will be observed that the limit of the reaction of cyanogen iodide on potassium iodide is reached at a concentration not exceeding N/100 for each. Hence the mixture of N/100 cyanogen iodide, N/100 potassium iodide, and 0.1 per cent starch solution in equal proportions by volume furnished us with a reagent upon which to test the conduct of different acids.

The tests upon acids were conducted in the following manner: To 1 cc. of the acid to be tested there was added, in the order named, 1 cc. N/100 potassium iodide, 1 cc. 0.1 per cent starch solution, and 1 cc. N/100 cyanogen iodide. In order to make more certain of the results, control experiments were carried out at intervals, using 1 cc. of water in place of the acid, the other substances remaining the same. The following acids were employed in the experiments, *viz.*, hydrochloric, sulphuric, benzenesulphonic, *p*-nitrotoluenesulphonic, oxalic, butyric, and carbonic. The results of these tests for all the acids, except carbonic and sulphuric, are given in Tables II. and III.

Table II.

Name of acid.	Dilution.	Color of the mixed solution.
Hydrochloric	N/1000	Dark blue
"	N/4000	Very light blue
"	N/5000	Colorless
p-Nitrotoluenesulphonic	N/1000	Dark blue
"	N/4000	Very light blue
Benzenesulphonic	N/1000	Dark blue
"	N/5000	Colorless
Oxalic	N/1000	Dark blue
"	N/5000	Colorless
Butyric	N/1000	Dark blue
"	N/2000	" "
"	N/3000	Light blue
"	N/4000	Colorless

Similar experiments were tried, using N/50 instead of N/100 potassium iodide.[1] The results are given in Table III.:

[1] While N/50 potassium iodide has been found to react with the cyanogen iodide alone, it is nevertheless possible to employ it of this strength in testing for acids by this method, if the tests are properly controlled by experiments in which water is employed instead of the acid being tested. With water and potassium iodide of this dilution the blue color develops only slowly. With dilute acids iodide of starch is formed immediately.

Table III.

Name of acid.	Dilution.	Color of the mixed solution.
Hydrochloric	N/4000	Distinct blue
"	N/5000	" "
"	N/10,000	Colorless
"	N/50,000	"
p-Nitrotoluenesulphonic	N/4000	Distinct blue
"	N/5000	" "
"	N/10,000	Colorless
Benzenesulphonic	N/5000	Distinct blue
"	N/10,000	Light blue
Oxalic	N/5000	Distinct blue
"	N/10,000	Colorless
Butyric	N/4000	Distinct blue
"	N/5000	Colorless

It has been observed that the sensitiveness of the reagent depends a great deal on the purity of the cyanogen iodide. The compound employed in our experiments was prepared by two entirely different methods, *viz.*, by the action of iodine on mercuric cyanide in ether solution, and by subliming a mixture of potassium cyanide and iodine. While both specimens of the compound were purified by sublimation it was still found that the compound prepared by the latter method was more sensitive towards acids. With the compound prepared from mercuric cyanide the limit of the reaction, for most acids at least, was N/5000, whereas with the compound prepared from potassium iodide and iodine the limit of the reaction was reached only with N/10,000 acid.

At present we are unable to explain this difference in conduct on the part of the cyanogen iodide prepared by these two methods. Regardless of this, however, it has been found possible to recognize any one of the above-named acids, with the exception of carbonic, at a dilution of 1 gram molecular weight of the acid in 20,000 to 40,000 liters of water, taking into consideration, of course, the fact that an acid of any degree of dilution was further diluted four times when added to the reagent. Expressed somewhat differently, these acids have been recognized by means of this reagent in the following quantities:

Acid.	Parts per million.
Hydrochloric	1.8
Benzenesulphonic	7.9
p-Nitrotoluenesulphonic	10.85
Oxalic	3.15
Butyric	5.5

Or by means of the more sensitive reagent :

Sulphuric	1.225
Benzenesulphonic	3.95
Oxalic	1.56

Some idea of the delicacy of cyanogen iodide as a reagent for acids may be formed by a comparison with other indicators. The following data are taken from Trommsdorf's table,[1] showing the sensitiveness of the more common indicators towards acids :

Indicator.	Strength of indicator.	Volume of titrated fluid. cc.	Volume of acid required.	Parts per million of acid required. cc.
Azolitmin	1 : 100	100	1.2 cc. N/100 HCl	4.38
Cochineal	1 : 80	"	3.0 " " "	10.95
Congo red	1 : 100	"	0.7 " " "	2.55
Corallin	1 : 100	"	0.6 " " "	2.19
Fluorescein	1 : 100	"	0.5 " N/10 "	18.25
Litmus	1 : 10	"	0.05 cc. " "	1.82
Methyl orange	1 : 200	"	1.0 " N/100 "	3.65
Phenolphthalein	1 : 100	"	0.5 " " "	1.82
Rosolic acid	1 : 100	"	0.7 " " "	2.55

It will be observed, therefore, that by means of cyanogen iodide it is possible to recognize the same quantity of hydrochloric acid that can be detected by litmus and phenolphthalein. In fact, in the case of sulphuric, benzenesulphonic, and oxalic acids we have been able to recognize a quantity of acid equivalent to one-half of this amount of hydrochloric acid.

From the results thus far reached it would seem that the delicacy of the reaction is in no wise dependent on the affinity of the acid. At least such is the case for the dilutions at which we have worked thus far. The limit of the reaction for the strong acids, such as hydrochloric, sulphuric, benzene-

[1] Indicators and Test-papers, Cohn, pp. 220–222.

sulphonic, and *p*-nitrotoluenesulphonic, is nearly, if not quite, the same as for the weaker acids, oxalic and butyric.

Some idea of the delicacy of the reaction under consideration is also afforded by the conduct of the reagent towards carbonic acid. As is well known, the conduct of this acid towards most indicators is very uncertain. With the mixture containing equal amounts by volume of N/100 cyanogen iodide, N/100 potassium iodide, and 0.1 per cent starch solution we have obtained the following results with this acid :

Dilution.	Color of the mixed solution.
N/2	Dark blue
N/3	Blue
N/100	Distinct blue

It will be observed, therefore, that by means of this reagent we have been able to recognize the presence of 77 parts of carbonic acid per million, and in all probability this is by no means the limit of the reaction for this acid. Whether a very weak acid like carbonic will give the reaction at the very great dilutions at which it has been obtained with hydrochloric and other strong acids remains to be seen.

Cyanogen Iodide as a Reagent for Measuring the Hydrolysis of Salts.

In view of the ease with which very small amounts of acids can be recognized by means of cyanogen iodide, it occurred to us to test the conduct of the compound towards various salts, particularly towards those that were known to be hydrolyzed in aqueous solution. The tests were conducted after the manner already described for acids, *i. e.*, to 1 cc. of the given salt, at known dilution, there was added, in the order named, 1 cc. of N/100 potassium iodide, 1 cc. of 0.1 per cent starch solution, and 1 cc. of N/100 cyanogen iodide. The formation of the iodide of starch indicated the presence of free acid in the solution of the salt. The names of the salts that have thus far been tested, together with the dilutions at which they were employed, and all other data, are given in Table IV., in which are also to be found the results of these experiments :

Table IV.

Name of salt.	Dilution.	Color produced.	Time of reaction.
Alum	N/10	Dark blue	Instantly
Potassium sulphate	"	Colorless	10 minutes
Potassium nitrate	"	"	30 "
Zinc sulphate	"	Faint blue	30 "
Magnesium sulphate	"	Colorless	1 hour
Ammonium sulphate	"	"	1 "
Aluminium chloride	"	Dark blue	Immediately
Manganese sulphate	"	Faint blue	" (increasing slowly on standing)
Potassium chloride	"	"	Immediately (increasing slowly on standing)
Chrome alum	"	Dark blue	Immediately
Aluminium nitrate	"	"	1 minute
Cadmium chloride	"	Colorless	30 minutes
Ferrous sulphate	"	Dark blue	Immediately
Ammonium ferric sulphate	"	"	"
Ferric nitrate	"	"	"
Nickel sulphate	"	"	Gradually
Nickel ammonium sulphate	"	Light blue	"
Nickel potassium sulphate	"	"	"
Nickel nitrate	"	"	"
Cobalt nitrate	"	Colorless	After 3 hours
Cobalt ammonium sulphate	"	"	Immediately (on long standing it became blue)
Cobalt potassium sulphate	"	Light blue	Gradually

In order to determine whether any one of these salts brought about the formation of the iodide of starch as the result of oxidation, control experiments were tried in doubtful cases, in which 1 cc. of water was used instead of the N/100 cyanogen iodide, the other substances remaining the same. It was found as the result of these trials that the iodide of starch was formed with the following salts, *viz.*, ferric nitrate and ferric sulphate. Even with these salts, however, the production of the

iodide of starch is much slower when acting alone than in the presence of the cyanogen iodide, so that the hydrolysis of these salts in aqueous solution is indicated just as certainly as in the case of those that do not cause the formation of the iodide of starch by oxidation.

It is apparent from these results that such neutral salts as potassium nitrate, potassium sulphate, magnesium sulphate, and ammonium sulphate are not hydrolyzed in their aqueous solution. On the other hand, potassium chloride gave a blue color with the reagent. This exceptional conduct on the part of this neutral salt is probably to be accounted for by the supposition that cyanogen iodide reacts directly with potassium chloride with the production of cyanogen chloride and potassium iodide. This last would then react with any excess of cyanogen iodide remaining in the manner already indicated above.

According to the indications afforded by the new reagent, aluminium, chromic, ferrous, and ferric salts are hydrolyzed to a greater degree than those of any other metal or basic radical. Salts of nickel, cobalt, manganese, and zinc are hydrolyzed to a much less extent, and cadmium chloride not at all.

This last result is at variance with the results reached by Long[1] in his investigation of the inversion of cane sugar by salts. According to Long, cadmium chloride inverted cane sugar more rapidly than any other salt employed in his experiments. At present we are unable to account for this peculiar difference in the conduct on the part of cadmium chloride.

In view of the ease with which very small amounts of free acid may be recognized by means of cyanogen iodide, it occurred to us that possibly the reagent might be employed to measure the amount of hydrolysis of hydrolyzable salts. The attempt has been made, therefore, to determine the extent to which potassium alum is hydrolyzed at great dilution. This was done by comparing the color produced with 1 cc. of alum solution of known concentration with that produced by a known quantity of sulphuric acid. Two solutions were pre-

[1] J. Am. Chem. Soc., 18, 717.

pared, one containing one molecular weight in grams of alum in 100 liters of water, the other one-half of one molecular weight in grams of sulphuric acid. The dilution of the solution of alum may therefore be denoted by M/100, and that of the sulphuric acid by N/100 $(H_2SO_4)_{\frac{1}{2}}$. The acid was therefore equivalent to N/100 hydrochloric, and for equal volumes of solution was equivalent to one-sixth of the sulphuric acid contained in the alum as aluminium sulphate. These two solutions were employed as the basis for subsequent dilutions. The conduct of these very dilute solutions of alum and sulphuric acid was then tested towards the reagent (N/100 cyanogen iodide, N/100 potassium iodide, and 0.1 per cent starch paste) in the manner already described above. In the following table are given the results of this comparison:

Alum.			*Sulphuric acid.*	
Dilution.	Color produced with reagent.	A.	Color produced with reagent.	Dilution.
M/10,000	Dark blue	$>$	Light blue	N/10,000 $(H_2SO_4)_{\frac{1}{2}}$
M/20,000	Blue	$>$	"	" "
M/30,000	"	$>$	"	" "
M/40,000	"	$>$	"	" "
M/50,000	Light blue	$=$	"	" "
M/60,000	"	$<$	"	" "
M/70,000	"	$<$	"	" "

In column A of the above table the sign of greater or less and the sign of equality are used to indicate that the amount of iodide of starch produced by the alum at the given dilution is greater or less than, or equal to, that produced by the sulphuric acid. It is evident from these results that when acting on a mixture of 1 cc. N/100 cyanogen iodide, 1 cc. N/100 potassium iodide, and 1 cc. 0.1 per cent starch, 1 cc. of M/50,000 alum produces the same quantity of iodide of starch as 1 cc. of N/10,000 $(H_2SO_4)_{\frac{1}{2}}$. On another occasion, using different solutions, it was found that M/60,000 alum was equivalent to N/10,000 $(H_2SO_4)_{\frac{1}{2}}$. Hence it follows that at a dilution of 200,000 to 240,000 liters the hydrolysis of alum amounts to from 83 to 100 per cent. Unfortunately, but few, if any, measurements of the hydrolysis of salts at such great dilutions have ever been made, so that at present we have no

reliable data with which to compare our own results. It follows from the law of mass action, however, that if the hydrolysis of any salt is small it will increase very nearly proportionately to the square root of the dilution. Now, according to Long, 1.44 per cent of alum is hydrolyzed in the N/4 solution of this salt. If, therefore, the law of dilution held strictly for this salt at all concentrations, we would expect alum to be completely hydrolyzed at a dilution of 20,000 liters. Our results, therefore, would seem to be in harmony with the general theory of such processes. It should be borne in mind, however, that the chemical changes taken advantage of in the use of cyanogen iodide as an indicator are after all not as simple as they appear at first sight. Whether any of them are of such a nature as to introduce a disturbing factor into the equilibrium of the hydrolysis can only be determined by further investigation.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, February, 1903.

A METHOD FOR CALIBRATING BURETTES.

BY D. W. HORN AND ELIZABETH M. VAN WAGENER.

The following method of calibrating burettes requires no special form of apparatus. It has proven satisfactory for the usual volumetric work of students, and is sufficiently accurate for more exact work.

An arrangement of apparatus similar to that in the Hempel gas-burette or Lunge nitrometer is used. Two burettes are mounted in an upright position on a tall iron stand and their tips are joined by a piece of rubber tubing. One of them is clamped firmly while the other can be raised or lowered, at the same time being guided by clamps fastened at different points along the upright rod of the stand. The calibration of one of them in terms of the other is accomplished by keeping the one stationary and causing water to flow into it from the other and movable one, which is gradually raised. The calibration is duplicated by lowering the latter again and causing the water to flow back into it.

The relative calibration thus obtained can be converted into an "absolute" one, provided one of the two burettes is calibrated by weighing the water it delivers between selected marks along its scale.[1] A burette thus standardized may be used in all subsequent calibrations as the standard with which other burettes may be compared by the arrangement of apparatus and the method already described.

In testing this method relative calibrations have been carried out under a variety of conditions. Burettes of the Mohr and Schellbach type have been used, readings have been made with and without floats, and soft rubber tubing in different lengths, both red and black, has been tried. In some cases the complete experiment was made by one of us. In others, after a calibration had been made by one, the duplicate calibration was made by the other. Sometimes only duplicates were made and at others the same calibration was repeated four or five times in succession. The records of some of these experiments are given in the following tables:

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
1	50.00	0.00	0.00
2	48.00	2.00	2.00
3	46.00	4.00	4.00
4	44.00	6.00	6.00
5	42.00	8.01	8.00
6	40.00	10.04	10.04
7	38.00	12.02	12.02
8	36.00	14.03	14.03
9	34.00	16.01	16.01
10	32.00	18.00	18.00
11	30.00	20.00	20.00
12	28.00	21.99	21.99
13	26.00	23.98	23.98
14	24.00	25.99	25.99
15	22.00	27.99	27.99
16	20.00	29.99	29.99
17	18.00	31.96	31.96
18	16.00	33.97	33.97

[1] Mohr: Lehrbuch der chem. anal. Titrirmethoden, 7 Ed. (1896), 18–19, Fresenius: "Quant. Chem. Analyse," 6 Ed. (1900), Vol. I., 44; For calculations see Watts' Dictionary, Vol. I., p. 248.

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
19	14.00	35.96	35.96
20	12.00	37.94	37.93
21	10.00	39.93	39.92
22	8.00	41.90	41.90
23	6.00	43.90	43.90
24	4.00	45.90	45.90
25	2.00	47.89	47.89
26	0.00	49.88	49.88
		(v. W.)[1]	(v. W.)[1]

The stationary burette in this experiment was a Mohr burette with a glass stop-cock, and was fitted with an Erdmann float. The other was a simple Mohr burette without a stop-cock or float. The former had a scale 53 cm. long, and the latter, one 61.3 cm. long. The readings were made from one end of the scale to the other, and the duplicate readings were made from the other end back to the starting point. The exact adjustment of the water levels at 0 and 50 at the beginning of the calibration was made with filter-paper, as adjustments of liquids to the marks are made in pycnometers. The next experiment differs from this one only in that a similar burette, but one with a scale as short as is usually to be found in a laboratory, was substituted for the stationary burette in the previous experiment. The length of its scale was 46.3 cm.

The first and the duplicate readings were not made by the same person.

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
1	0.00	49.95	49.94
2	2.00	47.99	47.98
3	4.00	45.96	45.95
4	6.00	43.95	43.95
5	8.00	41.96	41.95
6	10.00	39.96	39.96
7	12.00	37.99	37.99
8	14.00	35.99	35.99
9	16.00	33.96	33.96

[1] Experiments are marked (v. W.) or (H.), according as they are carried out by one or the other of us.

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
10	18.00	31.95	31.95
11	20.00	29.95	29.95
12	22.00	27.96	27.97
13	24.00	25.96	25.97
14	26.00	23.97	23.97
15	28.00	21.97	21.98
16	30.00	19.97	19.97
17	32.00	18.02	18.02
18	34.00	16.02	16.02
19	36.00	14.02	14.02
20	38.00	12.01	12.01
21	40.00	10.00	10.00
22	42.00	8.00	8.00
23	44.00	6.00	6.00
24	46.00	4.00	4.00
25	48.00	1.98	1.98
		(v. W.)	(H.)

In the above experiments the same piece of rubber tubing was used. The next experiment was made with another piece of the same kind of tubing (red) but of a different length. Another simple Mohr burette with a scale-length of 55 cm. and the one with a glass stop-cock used in the first experiment were used. This, along with several other similar experiments, show that the rubber tubing is without influence so far as the duplication of results is concerned.

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
1	0.00	49.90	49.90
2	2.00	47.90	47.90
3	4.00	45.90	45.90
4	6.00	43.91	43.90
5	8.00	41.94	41.94
6	10.00	39.94	39.94
7	12.00	37.93	37.93
8	14.00	35.92	35.93
9	16.00	33.92	33.93
10	18.00	31.94	31.94
11	20.00	29.96	29.96
12	22.00	27.97	27.98
13	24.00	25.99	25.99
14	26.00	23.99	23.99
15	28.00	22.00	22.00
16	30.00	19.99	19.99

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
17	32.00	18.00	18.00
18	34.00	16.01	16.01
19	36.00	14.02	14.03
20	38.00	12.05	12.05
21	40.00	10.07	10.08
22	42.00	8.08	8.09
23	44.00	6.10	6.10
24	46.00	4.11	4.11
25	48.00	2.11	2.11
26	50.00	0.11 (v. W.)	0.11 (v. W.)

The next table shows a comparison of a long Schellbach burette (scale-length 63 cm.) with the Mohr burette used in the previous experiments. These burettes with long scales were used to aid in detecting any possible inaccuracies. Four successive calibrations were made.

Number of reading.	Readings on Schellbach burette.	Readings on other burettes. First series.	Second series.	Third series.	Fourth series.
1	49.50	0.14	0.12	0.12	0.12
2	47.50	2.17	2.15	2.15	2.15
3	45.50	4.19	4.17	4.17	4.18
4	43.50	6.20	6.18	6.18	6.18
5	41.50	8.17	8.15	8.15	8.16
6	39.50	10.19	10.17	10.17	10.18
7	37.50	12.17	12.17	12.17	12.16
8	35.50	14.16	14.14	14.14	14.16
9	33.50	16.12	16.11	16.12	16.11
10	31.50	18.10	18.10	18.10	20.08
11	29.50	20.08	20.08	20.08	22.07
12	27.50	22.07	22.07	22.06	24.07
13	25.50	24.07	24.07	24.06	26.07
14	23.50	26.08	26.07	26.07	28.07
15	21.50	28.08	28.07	28.07	30.07
16	19.50	30.08	30.07	30.07	32.07
17	17.50	32.07	32.06	32.07	34.06
18	15.50	34.06	34.06	34.06	36.07
19	13.50	36.07	36.07	36.07	38.08
20	11.50	38.08	38.07	38.08	40.07
21	9.50	40.06	40.06	40.06	42.05
22	7.50	42.06	42.06	42.06	44.07
23	5.50	44.07	44.07	44.07	46.10
24	3.50	46.09	46.09	46.10	48.10
25	1.50	48.10	48.10	48.10	
26	0.00	49.61 (H.)	(H.)	49.61 (H.)	(H.)

Having established that duplicate determinations made under different conditions agree, it seemed advisable to find out whethe. or not relative calibrations by the above method would lead to the same results as the absolute method. To this end a Mohr burette, with a glass stop-cock, was calibrated by weighing the water it delivered between the marks indicating every 5 cc. The results are given in the following table :

Readings on burette.	Weights of separate quantities of water delivered. Grams.	Total weights of water delivered. Grams.
0.00 to 5.00	4.975	4.975
5.00 to 10.00	4.973	9.948
10.00 to 15.00	4.980	14.928
15.00 to 20.00	4.999	19.927
20.00 to 25.00	4.996	24.923
25.00 to 30.00	4.997	29.920
30.00 to 35.00	4.976	34.896
35.00 to 40.00	4.967	39.863
40.00 to 45.00	5.016	44.879
45.00 to 50.00	5.053	49.932
(H.)	(H.)	

A second Mohr burette with a glass stop-cock was then calibrated against this one, the absolute calibration of which has just been given. In this case a piece of black rubber tubing 117 cm. long, with an external diameter of 7 mm. and an internal diameter of 4 mm., was used. The readings in both burettes were made by the meniscus.

	Readings on stationary burette. (Standard.)	Readings on calibrated burette. First series.	Duplicate series.
1	0.00	49.90	49.90
2	5.00	44.90	44.90
3	10.00	39.90	39.90
4	15.00	34.90	34.90
5	20.00	29.92	29.92
6	25.00	24.96	24.96
7	30.00	19.93	19.93
8	35.00	14.96	14.96
9	40.00	9.94	9.94
10	45.00	4.91	4.91
		(v. W.)	(v. W.)

This second burette was then calibrated by the absolute method. The water was drawn as nearly as possible from between the numbers on its scale gotten by the relative calibrations just given.

Readings on burette.	Weights of separate quantities of water delivered. Grams.	Total weights delivered. Grams.
4.91 to 9.90	4.975	4.975
9.90 to 15.00	5.051	10.026
15.00 to 19.90	4.889	14.915
19.90 to 25.00	5.093	20.008
25.00 to 29.90	4.935	24.943
29.90 to 34.90	5.019	29.962
34.90 to 39.90	4.964	34.926
39.90 to 44.90	4.976	39.902
44.90 to 49.90	4.995	44.897
(H.)	(H.)	

Reference to the table of the relative calibrations of this burette will show that the water delivered by it between the marks 4.91 and 49.90 should weigh the same as the water delivered by the other burette between the marks 0.00 to 45.00 on its scale. The experiment has been given which shows that the first burette delivers 44.879 grams from 0.00 to 45.00, and the experiment just given shows that the second burette delivers 44.897 grams from 4.91 to 49.90. The difference is 0.018 gram.

The next table makes possible a comparison of the delivering capacity of the second burette as predicted upon the basis of the five relative calibrations against the first burette as a standard. This first burette, it will be recalled, was calibrated by the absolute method.

The accuracy which this table indicates could doubtless be increased by making the readings with a cathetometer. We consider it sufficiently accurate without this aid, for the error in reading burettes, such as are in general use, cannot fairly be considered as less than ± 0.01 cc.

We anticipated this accuracy in the method. In principle, the errors involved in its application should not exceed those necessary in reading burettes. It permits each point in the calibration to be fixed as accurately as the most sensitive re-

Readings on standard burette.	Corresponding readings on uncalibrated burette, gotten by relative calibrations. (W.)	Corresp'd'g weight of water delivered by standard burette. Grams. (H.)	Corresp'd'g weight of water delivered by uncalibrated burette. Grams. (H.)	Difference between weight predicted and weight found. Grams.	Total weights of water delivered by standard burette. Grams.	Corresponding total weights of water delivered by uncalibrated burette. Grams.	Difference between total weights delivered. Grams.
0.00– 5.00	49.90–44.90	4.975	4.995	0.020	4.975	4.995	0.020
5.00–10.00	44.90–39.90	4.973	4.976	0.003	9.948	9.971	0.023
10.00–15.00	39.90–34.90	4.980	4.964	0.016	14.928	14.935	0.007
15.00–20.00	34.90–29.92	4.999	4.999	0.000	19.927	19.934	0.007
20.00–25.00	29.92–24.96	4.996	4.995	0.001	24.923	24.929	0.006
25.00–30.00	24.96–19.93	4.997	5.023	0.026	29.920	29.952	0.032
30.00–35.00	19.93–14.96	4.976	4.959	0.017	34.896	34.911	0.015
35.00–40.00	14.96– 9.94	4.967	4.971	0.004	39.863	39.882	0.019
40.00–45.00	9.94– 4.91	5.016	5.015	0.001	44.879	44.897	0.018

versible end-reaction for which the burettes may be subsequently used, for by simply changing the relative levels back and forth one may fix each reading beyond readable error. The practice of duplicating by running the water, and the readings, backward through the same series of measurements balances errors that may arise from the necessarily unequal rates at which the water is delivered from one burette to the other between the different readings, thus insuring that no more than the normal amount of water has been left behind on the burette walls at any point, and furnishing duplicate readings whose agreement does not depend upon an accidental equality in the rate at which the two calibrations are made. It is, lastly, free from errors that may enter a method that depends upon the use of rubber tubing under different pressures. For example, when a piece of rubber tubing, such as we have used, 5 cm. long and closed at one end, is joined to the tip of a burette with a glass stop-cock, and both the burette and tubing are entirely filled with water, there is a readable difference in the level of the water, depending upon whether its weight is supported by the glass (when the stop-cock is closed) or by the rubber (when the stop-cock is opened). Such errors are variable and may be reduced, doubtless, by using thick rubber tubing and by having as few joints as possible made with it, but the method we have described avoids such errors entirely.

The precautions we have observed in the use of the method are not many. We have avoided the use of a float in the burette that is moved up and down in the course of a calibration, for it is well known that a float may readjust itself under the influence of changes in the position of a burette so that its axis is at quite a different angle to the axis of the burette from what it was originally. We have used a piece of tubing that was not too short. If the tubing is so short, or the burettes mounted so far apart that, in any of the positions they assume in the course of a calibration, the rubber is drawn or stretched, it is to be expected that errors may enter. Our general practice has been to so select the length of tubing and so arrange the burettes that beneath each a length of about 20

cm. always hangs vertically. We have always arranged the apparatus near the edge of a table-top so that the tubing hangs free beneath the burettes, and throughout the calibration does not come in contact with anything that might help support its weight or alter its volume. Lastly, we have made the duplicate calibration soon after the first one, for it is to be expected that if a sufficient time be allowed to intervene between the two sets of measurements the walls of the burette that is almost empty would dry and in the duplicate calibration the burette would seem to hold as much too much water as would be required to wet its walls again.

By this method it is possible to calibrate at as many or few points as may be desirable. The average time required to calibrate a burette at every 2 cc. and to duplicate it with the accuracy described in this paper, is about one and a half hours.

The same principle can, of course, be used in calibrating pipettes, and for the graduation of apparatus made for special volumetric purposes.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
March 4, 1903.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

V.—THE ACTION OF ALKALINE SULPHIDES UPON *p*-NITROBENZYLANILINE.

BY FREDERICK J. ALWAY AND ARTHUR B. WALKER.

p-Nitrobenzylaniline has been shown to undergo simultaneous reduction and oxidation when treated with alkaline sulphides in alcoholic solution,[1] *p*-amidobenzylideneaniline being formed. The reduction has been considered to take place according to the following equation:

$$2NO_2.C_6H_4.CH_2.NH.C_6H_5 + Na_2S = Na_2SO_4 + 2NH_2.C_6H_4.CH : N.C_6H_5.$$

While preparing *p*-amidobenzylideneaniline by the above method we noticed that in one case crystals of *p*-azoxybenzylideneaniline were formed, while in many previous preparations

[1] Chem. Centrbl., 1899, I., 238; D. R. P., No. 99,542.

there had been no formation of crystals, *p*-amidobenzylideneaniline being soluble in alcohol. The investigation on which we now report was undertaken in order to determine the conditions under which alkaline sulphides convert *p*-nitrobenzylaniline into *p*-azoxybenzylideneaniline.

We have found that when the sulphide is allowed to act upon the nitrobenzylaniline in the proportion of 1 molecule of the former to 8 molecules of the latter, the alcoholic solution being kept very gently boiling, the maximum yield of *p*-azoxybenzylideneaniline is obtained, *viz.*, about 75 per cent of the theoretical amount. With an increasing proportion of sulphide the yield steadily diminishes until only *p*-amidobenzylideneaniline is obtained. The insoluble *p*-azoxybenzylideneaniline, when boiled for some time with an alcoholic solution of sodium sulphide, is converted into a compound similar in properties and reactions to *p*-amidobenzylideneaniline. The formation of *p*-azoxybenzylideneaniline by the action of caustic alkalies upon the alcoholic solution of *p*-nitrobenzylaniline was likewise investigated quantitatively in order to determine the proportions required to produce the maximum yield. This is obtained when the substances are used in the proportion of 1 molecule of alkaline hydroxide to 4 molecules of *p*-nitrobenzylaniline. An increased proportion of alkali does not increase the yield, but, on prolonged boiling, decomposes the *p*-azoxybenzylideneaniline already formed. When it is desired to obtain the last-mentioned compound, the use of the caustic alkali is much to be preferred on account of the rapidity and certainty of its action.

Incidentally, we have endeavored to determine the best method of preparing *p*-nitrobenzylaniline, avoiding as far as possible the formation of *bis*-*p*-nitrobenzylaniline. Strakosch[1] prepared the former compound by heating a mixture of *p*-nitrobenzyl chloride and an excess of aniline to boiling for a few minutes. He isolated only the one compound. Paal and Sprenger[2] have since obtained the same compound, together with *bis*-*p*-nitrobenzylaniline, by heating *p*-nitro-

[1] Ber. d. chem. Ges., 6, 1062.
[2] *Ibid.*, 30, 69.

benzyl chloride (1 molecule) with aniline (2 molecules) in concentrated alcoholic solution for six hours. The solid obtained by pouring the crude reaction-mixture into cold water was separated by treatment with hot dilute alcohol into its component compounds, the *bis-p*-nitrobenzylaniline remaining undissolved. They obtained 70 per cent of the theoretical yield of *p*-nitrobenzylaniline and a small yield of the other compound, the amount not being given. Not long since one of us[1] showed that *p*-azoxybenzylideneaniline and the three analogous toluidines may be obtained in equally good yield directly from *p*-nitrobenzyl chloride, aniline or a toluidine, and a caustic alkali, if the mixture is heated to boiling one minute. We have now found that a prolonged heating of the two compounds is not necessary in order to obtain the maximum yield of *p*-nitrobenzylaniline. If the mixture of the two, in the proportions used by Paal and Sprenger,[2] be heated on the water-bath for two or three minutes, the yield of *p*-nitrobenzylaniline is 92 per cent of the theoretical amount, and that of *bis-p*-nitrobenzylaniline only from 1 to 2 per cent. When the mixture of *p*-nitrobenzyl chloride and aniline, without addition of alcohol, is heated to boiling it is necessary to have a great excess of aniline. In all cases, however, small amounts of *bis-p*-nitrobenzylaniline are formed. Under various circumstances this dissolves in ordinary alcohol and, therefore, is liable to escape detection.

No sulphate was detected in the reaction-mixtures obtained by boiling *p*-nitrobenzylaniline or *p*-azoxybenzylideneaniline with an alcoholic solution of sodium sulphide. The explanation of the reduction, referred to above, is evidently incorrect.

EXPERIMENTAL.

Preparation of p-Nitrobenzylaniline.

The method of Paal and Sprenger was first tried. A mixture of *p*-nitrobenzyl chloride (1 mol.) and aniline (2 mols.) was dissolved in the minimum quantity of alcohol (95 per cent) and heated on the water-bath for six hours. After re-

[1] Ber. d. chem. Ges., **35**, 2435.
[2] *Loc. cit.*

peated preparations by this method it was found that, while the solution usually remained clear until the end, at times after the heating had continued about five hours, large crystals of *bis-p*-nitrobenzylaniline began to separate out, and at the end of another hour the solution contained very little of this compound. When the reaction-mixture was poured into ice-water and the solid, so obtained, was treated with boiling ordinary alcohol, the whole of it dissolved. By continuing the boiling with alternate additions of water and alcohol, the *bis-p*-nitrobenzylaniline was caused to separate out as a yellow powder. It proved more satisfactory to treat the crude product with 70 per cent alcohol. This dissolved the *p*-nitrobenzylaniline and only a very small quantity of the other compound. One gram of *bis-p*-nitrobenzylaniline dissolved in 1200 cc. boiling 70 per cent alcohol. On cooling 0.35 gram separated from the solution.

When a mixture of *p*-nitrobenzyl chloride (1 mol.) and aniline (2 mols.) was heated on the water-bath it first melted to a clear liquid of a brownish-red color. Within two minutes this liquid became semi-solid on account of the formation of aniline hydrochloride. This compound, after being filtered out and washed with ether, was identified by its melting-point and its reactions. The hydrochloride of *p*-nitrobenzylaniline could not be detected in the reaction-mixture. When, instead of warming the mixture on the water-bath, it was heated in a flask over a flame, the reaction was the same when the temperature was not raised above 120°. But, as soon as it was raised above this point, without further application of heat, the temperature rose rapidly to 185°, the mass becoming an intense red in color. As we were unable to isolate *p*-nitrobenzylaniline from this red mass we have not investigated it further. When the temperature was not allowed to rise above 140° none of the red substance was formed. When a great excess of aniline (4 to 6 mols.) was used and the whole heated to boiling (one to two minutes) the same good yield, about 92 per cent, of *p*-nitrobenzylaniline was obtained. The excess of aniline was removed either by treatment with dilute aqueous hydrochloric acid or by distillation with steam, the *p*-nitro-

benzylaniline being insoluble in the dilute acid and non-volatile with steam. In an experiment that was performed to determine the yield of *p*-nitrobenzylaniline, *p*-nitrobenzyl chloride (10 grams) was mixed with aniline (11.2 grams) and heated on the water-bath five minutes. The semi-solid reaction-product was treated with boiling 70 per cent alcohol. The yield of *bis*-*p*-nitrobenzylaniline was 0.15 gram. The crystals of *p*-nitrobenzylaniline weighed 9.5 grams. To determine the amount of the last compound remaining dissolved in the alcoholic filtrate, the latter was heated and then treated with alcoholic potash. The *p*-azoxybenzylideneaniline so obtained weighed .2 grams. Ten grams of pure *p*-nitrobenzylideneaniline, under similar treatment, yielded 7.5 grams *p*-azoxybenzylideneaniline. The filtrate must have contained 2.7 grams of the former compound in solution. Accordingly, 10 grams of *p*-nitrobenzyl chloride yield 12.2 grams of *p*-nitrobenzylaniline, or 92 per cent of the theoretical amount.

Action of Caustic Alkalies upon p-Nitrobenzylaniline.

When the hot solution of this compound in ordinary or in absolute alcohol is treated with sodium hydroxide or potassium hydroxide in the solid form, or in either aqueous or alcoholic solution, or with sodium or potassium ethylate, the solution very rapidly darkens in color. When it has become almost black a very rapid separation of lustrous golden-yellow crystals takes place. At the end of a few minutes the reaction is complete. Small quantities of *p*-nitrobenzylaniline may be detected by this reaction. The crude reaction-products containing *p*-nitrobenzylaniline may be used in the same manner, without previous purification. In the latter case, however, it is necessary to use dilute alcohol as a solvent and to add an extra amount of alkali in order to neutralize the hydrochloric acid which occurs in the mixture as aniline hydrochloride. Hot alcoholic solutions of *p*-nitrobenzylaniline were treated with potassium hydroxide solution and the resulting *p*-azoxybenzylideneaniline was filtered out, washed well with alcohol, dried, and weighed. The yield reached a maximum when

the compounds were used in the proportion indicated above, *viz.*, 1 molecule of the hydroxide to 4 of the other compound. When smaller proportions of alkali were used, unchanged *p*-nitrobenzylaniline could be obtained from the filtrate. By prolonged heating of the *p*-azoxybenzylideneaniline with an excess of alkali it was entirely decomposed, forming a red solution, which, on treatment with water, gave a red precipitate.

Action of Alkaline Sulphides upon p-Nitrobenzylaniline.

The gently boiling alcoholic solution of *p*-nitrobenzylaniline was treated with an alcoholic solution of sodium sulphide, only small amounts being added at a time. Within from three to ten minutes the characteristic separation of crystals of *p*-azoxybenzylideneaniline began. They separated out much more slowly than when the alkaline hydroxides were used. The maximum yield was obtained when the two compounds were used in the proportion of 8 molecules of the former to 1 of the latter. When a higher proportion of sodium sulphide was used the yield was less and usually no separation of crystals took place. *p*-Azoxybenzylideneaniline was dissolved by prolonged boiling with sodium sulphide and alcohol. The solution gave a precipitate with water. In properties and reactions this was similar to *p*-amidobenzylideneaniline. To have fully identified this compound an analysis would have been necessary. This was not made. The alcoholic filtrates obtained by the action of sodium sulphide upon the above-mentioned compounds were evaporated to dryness and the residues treated with hot water. The clear aqueous filtrates gave no precipitate with barium chloride.

UNIVERSITY PLACE, NEBRASKA,
March 14, 1903.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

VI.—THE RELATIONS EXISTING BETWEEN THE PHYSICAL PROPERTIES AND THE MOLECULAR WEIGHTS OF *p*- AND *m*-NITROSOBENZALDEHYDE.

By Frederick J. Alway and Walter D. Bonner.

A year since, in an article by Alway and Welsh,[1] it was pointed out that while *m*-nitrosobenzaldehyde forms white crystals and is readily volatile with steam, the isomeric *p*-nitrosobenzaldehyde forms yellow crystals and at times cannot be distilled with steam, but passes over rapidly when, by the addition of calcium chloride, the temperature of the mixture in the flask through which steam is being passed is raised to the melting-point of *p*-nitrosobenzaldehyde, *viz.*, 137°. Likewise, this compound was found to volatilize readily when its green solutions, *e. g.*, in acetic acid and in alcohol, were subjected to the action of steam. It was mentioned, also, that both aldehydes are green in the liquid state and in solution, and that when volatilized with steam they give the characteristic odor of nitroso compounds.

Since that time Piloty[2] has practically completed the proof of the dependence of the green or blue color upon the monomolecular condition and of the white or colorless form upon the dimolecular condition. A large number of aliphatic nitroso compounds have been prepared by Piloty, and many more aromatic nitroso compounds by Bamberger and others. So far as we are aware, *p*-nitrosobenzaldehyde is the only compound in which a nitroso group is attached to a carbon atom, that is known to exist in the form of yellow crystals. For this reason it seemed desirable to determine its molecular weight both in cold and in hot solutions.

Piloty,[3] in describing some new nitroso compounds in 1898, stated that "these nitroso compounds, like all known substances of this class, show the ability to form colorless solids,

[1] J. Am. Chem. Soc., **24**, 1052 (1902).

[2] Ber. d. chem. Ges., **35**, 3090; Piloty and Stock: *Ibid.*, **35**, 3093; Piloty and Steinbock: *Ibid.*, **35**, 3101. See also Schmidt: *Ibid.*, **35**, 2323, 3727, 3737.

[3] *Ibid.*, **31**, 218 (1898).

which, in solution and in the liquid state, are an intense blue (or green) in color, a property which can be used for the recognition of true nitroso compounds, and which was first observed by Victor Meyer in the case of the pseudonitrols." (This statement was not correct, as the exception, *p*-nitrosobenzaldehyde[1] had already been described.) Soon after, the same investigator obtained brom-2-nitroso-2-propane[2] as a blue liquid at ordinary temperatures and, further, showed that, when in the colorless form, the nitroso compounds are able to form colorless solutions, the freezing-points of which indicate a dimolecular condition, but that, on warming, the color changes to blue or green, the molecular weight determinations of the latter showing that the monomolecular condition prevailed. About the same time Brühl,[3] finding that a 53 per cent supersaturated alcoholic solution of nitrosobenzene did not possess as intense a green color as 22 and 12 per cent solutions of the same compound in benzene, suggested that in the latter the nitrosobenzene was in a monomolecular condition and in the former in the dimolecular condition, as expressed by the formula :

$$C_6H_5.N.O$$
$$O.N.C_6H_5$$

He found the molecular refraction to agree with this assumption and suggested that there was a direct connection between the green color of nitroso compounds in general and the monomolecular condition. Bamberger and Rising[4] have determined the molecular weights of a large number of nitroso compounds and have found that those that form deep-green solutions in the cold contain simple molecules both in boiling and in freezing solutions. On the other hand, nitrosomesitylene and 2.6-dimethylnitrosobenzene, which form faintly green solutions in the cold, the latter becoming an intense green on warming, exist chiefly in the dimolecular condition in cold solutions but in the monomolecular condition in hot solutions.

[1] Ber. d. chem. Ges., **29**, 3037 (1896).
[2] *Ibid.*, **31**, 452, 457 (1898).
[3] *Ibid.*, **31**, 1465 (1898).
[4] *Ibid.*, **33**, 3877 (1901).

A few nitroso compounds form blue or green crystals, *viz.*, 3.4-dimethylnitrosobenzene,[1] brom-2-nitroso-2-dimethyl-3.3-butane,[2] *o*-nitrosoanisol, *p*-nitrosoanisol,[3] 1.4-dibrom-1.4-dinitrosocyclohexane, and 1.4-dichlor-1.4-dinitrosocyclohexane.[4] The last-mentioned compound, under the influence of hydrochloric acid, changes to the isomeric 1.4-dichlor-1.4-*bis*-nitrosylcyclohexane. The latter is colorless and does not form a green liquid or green solutions. It is considered by Piloty[5] to form the transition between those dimolecular nitroso compounds that decompose into monomolecular nitroso compounds only in boiling solutions, and the *bis*-nitrosyl compounds, like *bis*-nitrosylbenzyl[6] and *bis*-nitrosylcarvon,[7] which are odorless and non-volatile, and are blue or green neither in solution nor in the liquid state.

We have found that in boiling benzene both the *p*- and the *m*-nitrosobenzaldehyde show the normal molecular weight. The same is true in freezing acetic acid. In freezing benzene the former shows the monomolecular condition, but the latter gives evidence of a part being in the dimolecular condition. The decrease in the intensity of the green color of the solution of *m*-nitrosobenzaldehyde in benzene as the freezing-point of the latter is approached is in accord with the change in molecular weight. A change in the intensity of the color of solutions of *p*-nitrosobenzaldehyde, on the other hand, is accompanied by the separation of yellow crystals. The molecular weight determinations show that *m*-nitrosobenzaldehyde, rather than *p*-nitrosobenzaldehyde,[8] resembles nitrosomesitylene. No light is thrown by these determinations, however, upon the cause of the peculiar position that *p*-nitrosobenzaldehyde occupies among the nitroso compounds.

In experiments 5, 6, and 7 the compound dissolved very slowly in cold benzene. After the addition of the first weight

[1] Ann. Chem. (Liebig), **316**, 285 (1901).
[2] Piloty: Ber. d. chem. Ges., **35**, 3092 (1902).
[3] v. Baeyer and Knorr: *Ibid.*, 3034 (1902).
[4] Piloty and Steinbock: *Ibid.*, **35**, 3101 (1902).
[5] *Ibid.*, **35**, 3101 (1902).
[6] Ann. Chem. (Liebig), **263**, 212.
[7] v. Baeyer: Ber. d. chem. Ges., **28**, 642 (1895).
[8] J. Am. Chem. Soc., **24**, 1054 (1902).

Experiment number.	Solvent.	Dissolved substance.	Weight of solvent in Grams.	Weight of dissolved substance in Grams.	Percentage strength of solution.	Depression of freezing-point.	Elevation of boiling-point.	Molecular weight.
1	Benzene	*p*-Nitrosobenzaldehyde	107.2478	0.5938	0.554		0°.120	124.7
2	"	"	"	1.9596	1.83		0°.360	137.4
3	"	"	"	2.6912	2.51		0°.495	136.9
4	"	"	"	3.2404	3.02		0°.605	134.9
5	"	"	17.2762	0.1004	0.581	0°.250		116.2
6	"	"	"	0.1506	0.871	0°.345		123.7
7	"	"	"	0.2588	1.50	0°.590		127.1
8	Acetic acid	"	20.5882	0.1280	0.622	0°.215		112.4
9	"	"	"	0.2110	1.025	0°.335		119.3
10a	"	"	"	0.3140	1.53	0°.365		163.4
10b	"	"	"	"	"	0°.525		113.7
11	Benzene	*m*-Nitrosobenzaldehyde	116.1494	0.7142	0.615		0°.130	127.7
12	"	"	"	0.9932	0.855		0°.170	135.8
13	"	"	"	1.3196	1.136		0°.215	142.7
14	"	"	"	1.5855	1.365		0°.260	141.8
15	"	"	17.2762	0.0602	0.348	0°.105		165.9
16	"	"	"	0.0968	0.560	0°.165		169.7
17	"	"	"	0.1438	0.832	0°.310		134.2
18	"	"	"	0.2658	1.538	0°.570		134.9
19	Acetic acid	"	20.5882	0.0672	0.336	0°.110		115.6
20	"	"	"	0.1484	0.721	0°.225		124.9

Theoretical molecular weight of nitrosobenzaldehyde = 135.

and continued stirring for one hour very little had dissolved. A determination of the freezing-point showed a depression of 0°.05. Then the solvent was warmed to about 60° to dissolve the substance. This had to be repeated after the addition of each new portion. No crystals separated from the solution on cooling.

In experiment 10a crystals separated out before the solution began to solidify. The whole was warmed until the crystals redissolved and then cooled down again (Experiment 10b). No separation of crystals of the dissolved substance took place in this case.

In Experiments 15, 16, 17, and 18 the solvent was warmed to dissolve the nitrosobenzaldehyde. In 15 and 16 the color of the solution, which was a deep green when warm, became much fainter as the temperature approached the freezing-point of the solvent, but returned to its former intensity on warming. In Experiments 17 and 18 no such change in the color was observed.

Naphthalene is not available as a solvent in the molecular weight determinations of the nitrosobenzaldehydes, as the green color of the solutions rapidly changes to a red, showing that a chemical change has taken place. A similar change takes place when the aldehydes are boiled with benzene for a long time.

Saturated solutions of the two nitrosobenzaldehydes in ether, benzene, and acetic acid were prepared. Part of each was heated to boiling and another part cooled to 0°. The only case in which a distinct change in the color was noticeable was that in which the benzene solution of *m*-nitrosobenzaldehyde was cooled, the green color becoming much fainter.

UNIVERSITY PLACE, NEBRASKA,
April 25, 1903.

THE ACTION OF PHOSPHONIUM IODIDE ON POLYCHLORIDES.[1]

[FIRST PAPER.]

BY ERNESTINE AND PETER FIREMAN.

Since Liebig,[2] in 1832, took up the study of the action of gaseous ammonia or ammonium chloride on phosphorus pentachloride, a study which led him to the discovery of "chlorophosphuret of nitrogen," a number of chemists[3] have, from time to time, attacked this subject. However, until very recently, little light was thrown on the reaction in question. The yield was very bad, and the relation of the chlorophosphuret to other phosphorus compounds remained unestablished. Our knowledge of the products of the action of sal ammoniac or gaseous ammonia on the pentachloride of phosphorus was in this unsatisfactory state when H. N. Stokes, in 1895, began the investigation of this subject. One of the first results of his investigation[4] was the isolation, from the products of the reaction, of a new chloronitride with the composition $(PNCl_2)_4$ and of an oily chloronitride with the same percentage composition, whose molecular weight remained undetermined. These two bodies were obtained in addition to Liebig's chlorophosphuret $(PNCl_2)_3$. In his earlier experiments Stokes prepared the chloronitrides of phosphorus by the method, described by Gladstone,[5] of distilling phosphorus pentachloride with a large excess of ammonium chloride. But in 1897 he devised a new method[6] which gives an almost theoretical yield. It consists in heating a mixture of ammonium chloride and phosphorus pentachloride in the proportion of their molecular weights in a sealed tube. From the reaction-products Stokes was able to isolate, by distilla-

[1] The present communication contains a part of the results of an investigation carried out in 1900, at the Columbian University, Washington, D. C.

[2] Ann. Chem. (Liebig), **11**, 146.

[3] In his first article "on the chloronitrides of phosphorus" (This JOURNAL, **17**, 275) H. N. Stokes quotes the literature on this subject.

[4] *Loc. cit.*

[5] Q. J. Chem. Soc., **3**, 135; Ann. Chem. (Liebig), **76**, 76.

[6] This JOURNAL, **19**, 782.

tion under diminished pressure, the following series of polymeric chloronitrides:

$(PNCl_2)_3$, $(PNCl_2)_4$, $(PNCl_2)_5$, $(PNCl_2)_6$, $(PNCl_2)_7$, and $(PNCl_2)_x$.

In view of the smoothness of the reaction between phosphorus pentachloride and ammonium chloride and the remarkable nature of the resulting chloronitrides and of the products of their saponification, it has appeared desirable to determine by investigation whether we have here a unique reaction, without analogues, or a typical representative of a whole class. It has appeared desirable, in other words, to ascertain whether ammonium chloride would not act upon other inorganic polychlorides in a similar manner. On the other hand, it has seemed of interest to compare the action of a phosphonium halide upon polychlorides with that of ammonium chloride upon them. The former problem has been taken up by one of us and E. G. Portner, while the latter the present writers have attempted to study. The following is a description of some of the results obtained by them.

Since phosphonium chloride and phosphonium bromide are practically inaccessible in quantities necessary for an extended research, only phosphonium iodide is available for an investigation of this kind.

It must be confessed that at the inception of this research the hope was entertained that the action of phosphonium iodide upon the polychlorides would resemble to a greater or less extent that of ammonium chloride upon them. It was hoped that by treating bodies such as antimony pentachloride or tin tetrachloride with phosphonium iodide, compounds would result resembling the chloronitrides of phosphorus, but containing, in place of phosphorus, antimony or tin, and in place of nitrogen, phosphorus. This expectation appeared to be justified by the fact that a compound consisting of tin, phosphorus, and chlorine was described by R. Mahn,[1] who prepared it by the action of hydrogen phosphide upon stannic chloride. To be sure, the composition assigned to that body

[1] Jenaische Ztschr. f. Medicin u. Naturwiss., 3, 158.

was rather strange, *viz.*, $Sn_3P_3Cl_6$; but an incorrect formula was also ascribed to Liebig's chlorophosphuret for a long time. It therefore became an additional incentive to the carrying out of this investigation to verify, if possible, Mahn's results, and perhaps to correct the formula for the body he obtained.

Actual experiments soon demonstrated, however, that the action of phosphonium iodide on the polychlorides is radically different from that of ammonium chloride on these chlorides; that the analogues of the chloronitrides, with phosphorus in place of nitrogen, cannot, if at all, be prepared through the aid of phosphonium iodide. However, the action of phosphonium iodide on the tetra- and pentachlorides, such as it is, has appeared well worthy of careful study.

In accordance with the original object of this investigation, the lowest polychlorides[1] which could fall within its scope are the tetrachlorides. The common tetra- and pentachlorides were, therefore, first attacked, but the nature of the results obtained seems to justify the extension of this study so as to include also some lower polychlorides.

I.

Action of Phosphonium Iodide on Antimony Pentachloride.

The experiments described below show that when phosphonium iodide and antimonic chloride are heated in a sealed tube a reaction takes place between them which can be represented by the following equation:

$$3SbCl_5 + 3PH_4I = SbI_3 + 2SbCl_3 + 9HCl + PH_3 + P_2.$$

[1] It is evident that for a reaction similar to that which takes place between phosphorus pentachloride and ammonium chloride, no lower chlorides than tetrachlorides can be used in place of phosphorus pentachloride. For, as Stokes shows, the chloronitrides of phosphorus result according to this equation:

$$PCl_5 + NH_4Cl = 4HCl + PNCl_2.$$

Now, with ammonia, which can be used in place of ammonium chloride, the reaction must be as follows:

$$PCl_5 + NH_3 = 3HCl + PNCl_2.$$

Hence it is obvious that only chlorides of such elements which carry at least 4 atoms of chlorine to 1 of their own, can give off 3 atoms of chlorine to form 3 molecules of hydrochloric acid with the hydrogen of ammonia, and still retain chlorine:

$$CCl_4 + NH_3 = 3HCl + CNCl.$$

In this reaction antimonic chloride is reduced to antimonous chloride, a third of the latter being converted into antimonous iodide, copious quantities of hydrochloric acid gas and some hydrogen phosphide are evolved, and phosphorus is set free.

Antimony pentachloride and phosphonium iodide, when brought together in the open air at ordinary temperature, act upon one another with explosive violence, and free iodine escapes with the other gases.

In order to seal up together antimonic chloride and phosphonium iodide, it is necessary to place one of these substances in a narrow tube, and then place this narrow tube within a larger tube, into which the other substance has been previously introduced.

In studying the reaction under consideration we proceeded as follows: The phosphonium iodide was placed in an ordinary bomb tube, into which the antimonic chloride, contained in a short, narrow tube, was then introduced. Digestion at the temperature of boiling water is sufficient to bring about the reaction indicated above. It is advisable, however, to heat at a somewhat higher temperature in order to hasten matters. It may perhaps be well to describe one experiment in detail.

Four tubes, each containing 3 cc. (6.8 grams) of antimony pentachloride (1 mol.) and 3.6 grams of phosphonium iodide (1 mol.), were heated for five hours at 95° to 105°. On cooling, the contents of the tube consisted of some unchanged phosphonium iodide (which remained at the bottom), of a solid mass partly orange-yellow and partly ruby-red in color, and of some liquid (apparently unchanged antimonic chloride). On opening the tubes, hydrogen chloride escaped. The loss of weight in the four tubes was 1.7, 1.6, 1.9, and 1.8 grams respectively.

On further digestion for five hours at 100° to 110°, the entire contents of the tubes became solid. No phosphonium iodide was now to be discerned, and the color of the mass was yellow and orange. On opening, the tubes were found to have lost 0.6, 0.65, 0.2, and 0.4 gram, respectively.

Heating for nine hours more at 100° to 110° caused in two of the tubes only an additional loss of 0.1 gram of gas. The total loss in the four tubes was 2.4, 2.25, 2.2, and 2.2 grams, respectively.

In other experiments the tubes were opened more frequently, and the gradual disappearance of the phosphonium iodide and antimony pentachloride could be well observed. The former remained at the bottom of the tube in an entirely detached mass from the rest of the substance, while the latter remained liquid, but was rendered dark in color. Some of the gas escaping, on opening the tubes, was collected each time in a flask, with some water, and examined. At the earlier stages nothing but hydrochloric acid escaped. The precipitate with silver nitrate was perfectly white and dissolved easily and completely in ammonia. Towards the end of the operation, at the last opening or two, the outrushing gas flashed up, thus showing the formation of phosphine.

Larger quantities of the material than were used in the tubes of the experiments described above can be heated in one tube with entire safety, but then the tubes must be opened more frequently and after shorter intervals. The digestion should be so regulated that not more than 2 grams of hydrochloric acid gas will be present at one time in a tube of medium capacity.

There being no other more convenient way to get out the product of the reaction from the tubes, the latter were cut into pieces, from which as much as possible of the substance was then scraped out and collected separately in a flask (these were styled Portion I.). The pieces of the tube, with what adhered to them (Portion II.), were placed in another flask. Portion II. was first treated with solvents. It, together with the pieces of glass, was covered with benzene and heated for some time in a water-bath with a reflux condenser. The liquid was then filtered hot into the flask containing Portion I. The residue of Portion II. was again digested with benzene with the reflux condenser, and the liquid filtered into the flask containing Portion I. This treatment was repeated once more. The benzene solution, together with the main portion

of the product, was now heated on the water-bath with a return condenser, and the liquid filtered hot into a flask. The residue was treated twice more with benzene. The united filtrates were then concentrated to about 300 cc. by distillation and then allowed to cool in a stoppered flask. Crystals separated which were mostly red in color, flat, and united into bands. Some small, yellow, square crystals were also formed. The liquid was poured off and the crystals, which weighed 5.5 grams, were redissolved in benzene and recrystallized. A red substance was obtained which, on drying in the desiccator, and for a short time in the steam-oven, proved to be pure antimony triiodide. It was identified by its melting-point (167°) and by analysis, as follows:

I. 0.3264 gram substance gave 0.1112 gram Sb_2S_3, corresponding to 0.0798 gram antimony.

II. 0.2442 gram substance gave 0.3412 gram AgI, corresponding to 0.1844 gram iodine.

	Calculated for SbI_3.	Found.
Sb	24.28	24.45
I	75.72	75.49

The filtrate, after the removal of the first crop of crystals (5.5 grams) was considerably concentrated by distillation and allowed to stand in a stoppered flask. After some time crystals separated, which were in the main yellow, but in a few instances red. The two kinds of crystals (aggregating 3 grams) proved to be two modifications of antimony triiodide. They showed the same melting-point (167°), and the yellow modification passed over into the red one when it was attempted to recrystallize it.

On further concentrating the mother-liquor, two more grams of antimonous iodide (identified by its melting-point) were obtained. The remaining solution was reduced to a small bulk and allowed to get cold. A white, crystalline cake formed. Instead of pressing out from the cake the remaining benzene and so separating the white crystalline mass from the mother-liquor by filtering with suction, all the benzene was distilled off and the solid mass transferred to a distilling-

flask. The latter operation was easily carried out by melting the residue by gently warming and then pouring. The white solid distilled over for the most part at about 224°. By its easy fusibility and its boiling-point it was shown to be antimonous chloride.[1] The last portion of the distillate was somewhat contaminated with some antimonous iodide which had remained to the last in the benzene solution, and which, though distilling at a much higher temperature (414° to 427°), sublimes at a considerably lower temperature. About 11 grams of antimonous chloride were obtained.

The residue which remained from the main portion of the product, after it was treated with benzene, as well as the one which remained from that portion of the product which adhered to the glass, was treated with carbon disulphide in a water-bath with a reflux condenser in order to remove the residue of antimonous iodide. The filtered solution gave, on concentration, about two more grams of the latter.

The final residue (the free one and the one adhering to the glass), was a bright-red powder which responded to the various tests for red phosphorus. It took fire when touched with a hot glass rod, and when heated in a small tube, closed at one end, it formed yellow phosphorus. It dissolved in nitric acid, and the solution, when treated with magnesia mixture in the usual way, gave the characteristic precipitate for phosphoric acid. A quantitative determination of the phosphorus was attempted, but, as is well known, the complete oxidation of red phosphorus is a very slow process. After repeated treatment with dilute and concentrated nitric acid, alternately, and evaporating to dryness, not more than about 70 per cent of phosphorus was found. It did not seem necessary to pursue the estimation of phosphorus any further, since even the imperfect analysis made proved that we had in hand phosphorus, although it was associated with the accumulated impurities of the various operations. About 1.5 grams of the red phosphorus were obtained from the main portion of the reac-

[1] The boiling-point of antimonous chloride is variously stated. It is given by some as 216° and by others as 223°.5. A perhaps not uninteresting observation was made in this laboratory which may explain this discrepancy. A freshly obtained quantity of antimony trichloride, which distilled over with great constancy at about 224°, showed, after a few weeks, with just as much constancy the boiling-point 216°.

tion-product. The phosphorus which adhered to the glass probably amounted to about 0.5 gram.

In concluding the description of the experimental part of the study of the action of phosphonium iodide upon antimony pentachloride, it may be added that the antimony was determined as Sb_2S_3 in the usual way, while the iodine was precipitated from a tartaric acid solution to which a weighed amount of silver nitrate in very slight excess was added.[1]

The experiments described above seem to be very satisfactorily represented by the equation :

$$3SbCl_5 + 3PH_4I = SbI_3 + 2SbCl_3 + 9HCl + PH_3 + P_2.$$

1. The antimonic chloride and phosphonium iodide were used in the proportion of 1 molecule to 1 molecule as required by the equation.

2. The antimony was actually obtained in the form of antimonous iodide and chloride, and only in this form. According to the equation, more of the iodide (mol. wt. 502.55) than of the chloride (mol. wt. $226.5 \times 2 = 453$) should be obtained. The actual quantities weighed were 12.5 grams of antimonous iodide and about 11 grams of antimonous chloride. As compared with the theoretical amounts of the two substances which should have been expected from the materials of the four tubes, only about 85 per cent of the iodide and 80 per cent of the chloride were obtained. But it must be remembered that the antimony chloride used was only the commercial article, and the phosphonium iodide can never be prepared in a state approximating purity; and further, that in the scraping out of the substances from the tubes and the many operations involved in the treatment of the products of the reaction, considerable loss of the substance could not be avoided.

3. The amount of hydrochloric acid gas which escaped is really decisive in the interpretation of the reaction. Under the most favorable conditions, a tube which contained 3.6 grams of phosphonium iodide and 6.8 grams of antimonic chloride lost 2.4 grams from the escape of gases. The theoretical

[1] J. P. Cooke : Proc. Am. Acad. of Arts and Sciences, [2], 5, 72.

loss of hydrochloric acid and hydrogen phosphide, according to the equation, should have been 2.7 grams. The loss found amounted to 90 per cent of the one calculated. A better agreement could not be expected considering the condition of the materials used.

4. Red phosphorus was obtained in sufficient quantities to satisfy the theory, and the formation of phosphine gas, which was observed in the later stages, can be assumed to have proceeded in accordance with the equation.

As was mentioned above, the antimony triiodide which forms in the reaction was obtained in two modifications, in a red and in a yellow one. It is interesting to note that from one and the same benzene solution, on gradual concentration, there first separated out red crystals exclusively, then followed a crop of mostly yellow crystals, then again red ones, and lastly, antimonous chloride, which remained somewhat contaminated with the red antimonous iodide.

The reaction between antimonic chloride and phosphonium iodide is, it appears, essentially a reducing one. All the antimonic chloride is reduced to the antimonous state. When equal numbers of molecules of the two reagents are used, a third of the antimonous chloride is converted into antimonous iodide.

The reducing properties of phosphonium iodide are well known, but we are not aware that it has as yet been at all made use of in this capacity in inorganic chemistry. And yet it would appear from the reaction just described that it may become serviceable to the inorganic chemist.

According to H. Rose,[1] antimonic chloride and phosphine form an addition-product, some hydrochloric acid gas being evolved at the same time. But R. Mahn,[2] in repeating Rose's experiment, failed to obtain the addition-product in question. He found instead that the two bodies act upon one another according to this equation:

$$4SbCl_5 + PH_3 = 4SbCl_3 + PCl_5 + 3HCl.$$

[1] Pogg. Ann., 24, 165.
[2] Jenaische Ztschr. f. Medicin u. Naturwiss., 3, 158.

II.

Action of Phosphonium Iodide on Phosphorus Pentachloride.

These two substances act upon one another even at ordinary temperatures, but the reaction does not seem to proceed much beyond the point of contact of the two bodies. When heated in a sealed tube they undergo the following reaction:

$$3PCl_5 + 3PH_4I = PI_3 + PCl_3 + 12HCl + P_4.$$

Not only is the pentachloride reduced to a lower halide, but a part of its phosphorus is also reduced to the elementary condition. In one experiment the formation of diphosphorus tetraiodide was observed, which probably resulted from a secondary reaction between the phosphorus triiodide and phosphorus.

The progress of the reaction seems to be very much influenced by the circumstance as to whether the two substances are thoroughly mixed with one another before the digestion or not. In the former case one can observe, as an intermediate stage, the formation at about 80° C., of a liquid from which, if allowed to cool, short, fine needles separate. If no mixing took place the intermediate formation of a liquid was not observed.

The following are some of the experiments made with phosphonium iodide and phosphorus pentachloride:

Two tubes, each containing 2 grams of phosphonium iodide (1 mol.) and 2.6 grams of phosphorus pentachloride (1 mol.) were sealed and heated two and one-half hours at 90° to 100°. On cooling, in only one tube was any liquid noticed. On opening, an acid, non-inflammable gas escaped—hydrochloric acid; no phosphine, no hydriodic acid. The losses in weight were: (I.) 0.9 gram; (II.) 1 gram. On further heating for three hours at 100° to 110°, again only hydrochloric acid escaped and to the following extent: From (I.) 0.5 gram, and from (II.) 0.65 gram. The tubes were now digested for five hours at 120° to 125°, upon which they lost 0.35 gram and 0.25 gram of hydrochloric acid, respectively. Further digestion did not cause the evolution of any more gas. The prod-

uct was entirely solid, mostly red in color but to a small extent yellow.

In order to separate the phosphorus trichloride from the reaction-product in which it is present in but small quantity (theoretically to 2 grams of phosphonium iodide correspond 0.46 gram of the trichloride) we proceeded in one case as follows: The mass in the tube was treated with carbon disulphide which is said to dissolve freely both of the iodides of phosphorus as well as the trichloride of this element, and the solution distilled over a water-bath. For some reason or other no phosphorus trichloride (boiling-point 76°) was obtained.

The following method, however, proved successful for the separation of the trichloride: The tube containing the reaction-product was bent in the middle to almost a right angle, the tip sealed, and then the contents of the tube subjected to distillation. The lower half of the tube was immersed in boiling water while the upper half, with the tip, dipped into cold water. Recourse was had to distillation in a closed tube in order, by duplicating the conditions under which the reaction took place, to avoid possible interaction between the trichloride and the iodide of phosphorus. As a result of this distillation a sufficient quantity of a colorless liquid was obtained, to be easily identified as phosphorus trichloride. It became hot when a few drops of water were added to it, and the water solution so formed (phosphorous acid) reduced silver nitrate and mercuric chloride from their solutions.

Upon the removal of the phosphorus trichloride the contents of the tube were treated with carbon disulphide and the solution formed was filtered and concentrated, when short, red needles separated, which, by their melting-point of 55° C., were easily identified as phosphorus triiodide. The residue left after the treatment with carbon disulphide consisted of red phosphorus.

Conclusive evidence of the fact that the reaction between phosphonium iodide and pentachloride takes place as indicated by the equation given above, is supplied by the amount of hydrochloric acid liberated. The two tubes lost, respec-

tively, 1.75 and 1.9 grams of hydrochloric acid. According to theory they should have lost 1.83 grams.

In one experiment in which the digestion was finished at a higher temperature (135°), some well-shaped crystals were found in the upper part of the tube. A melting-point was taken and proved to be 110°, which is the melting-point of diphosphorus tetraiodide, P_2I_4.

On the whole, it may be stated that the reaction between phosphorus pentachloride and phosphonium iodide is similar in nature to that between the latter and antimony pentachloride. In both cases the phosphonium iodide acts as a reducing agent, but in the case of phosphorus pentachloride the reduction is more complete, for not only is the phosphorus pentachloride reduced to phosphorus trichloride (in a part of which the chlorine is replaced by iodine), but one-third of it is reduced to elementary phosphorus.

According to Mahn,[1] hydrogen phosphide acts on phosphorus pentachloride according to the equation:

$$PH_3 + 3PCl_5 = 4PCl_3 + 3HCl.$$

III.

Action of Phosphonium Iodide on Tin Tetrachloride.

In the study of the action of phosphonium iodide upon tin tetrachloride, the previous elucidation of the reaction between phosphonium iodide and antimony pentachloride, and between the former and phosphorus pentachloride, was of great advantage. But for the experience so gained we might have been led to an imperfect interpretation of what takes place when tin tetrachloride and phosphonium iodide are heated in a closed tube, for the first experiments seemed to point to the following reaction:

$$4SnCl_4 + 4PH_4I = SnI_4 + 3SnCl_2 + 10HCl + 2PH_3 + P_2.$$

As a matter of fact, the tin tetraiodide was obtained in considerable quantity and identified by a complete quantitative analysis. Moreover, the amount of hydrochloric acid and phosphide seemed to accord with the equation. But on com-

[1] Jenaische Ztschr. f. Medicin u. Naturwiss., 8, 158.

paring this reaction with that taking place between phosphorus pentachloride and phosphonium iodide,

$$3SbCl_5 + 3PH_4I = SbI_3 + 2SbCl_3 + 9HCl + PH_3 + P_2,$$

we were struck by the relative incompleteness of the former. It appeared strange that the stannic iodide was not reduced to stannous iodide. The digestion was, therefore, continued for longer periods of time and at higher temperatures with the result that the reduction was as complete as that which takes place when antimony pentachloride is treated with phosphonium iodide. Thus the reaction is really as follows:

$$6SnCl_4 + 6PH_4I = 3SnCl_2 + 3SnI_2 + 18HCl + 2PH_3 + 4P.$$

When tin tetrachloride and phosphonium iodide are brought together at ordinary temperatures a mild reaction sets in, which stops after a short time if the access of moist air is prevented. A steady reaction between the two bodies begins in the neighborhood of 100° C.

The following are some of the experiments made with tin tetrachloride and phosphonium iodide. In the first experiments the tin tetrachloride, contained in a short tube of small bore, was placed in one of a larger bore into which the phosphonium iodide had previously been introduced. Four tubes, each containing 6.5 grams (3 cc.) of tin tetrachloride (1 mol.), and 4 grams of phosphonium iodide (1. mol.) were digested four hours between 90° and 100° C. On cooling, a thin, orange-yellow sublimate, covering the whole inner surface of the tube, was to be observed. The most of the phosphonium iodide lay unchanged at the lower part of the tube and above it a black mass was formed. Only one tube (I.) was opened. Four-tenths gram of a non-inflammable acid escaped, which proved to consist of pure hydrochloric acid. On further treating for twelve hours at 112° to 115° C. the tube, which had lost 0.4 gram of hydrochloric acid, lost 0.5 gram more of the same gas. After heating for one-half hour longer at 120° to 125° tube II. gave off, on cooling, 1 gram and tube III. 0.9 gram of hydrochloric acid not contaminated with either hydriodic acid or phosphine. Tube I. was not opened this

time. One tube exploded. Further digesting for three and one-half hours at 120° to 125° caused the following losses of pure hydrochloric acid: Tube I. 0.8 gram, tube II. 0.7 gram, tube III. 0.6 gram. The sublimate inside the tube was orange-red. On continued heating for one and one-half hours at 125° to 135°, the losses were, I. 0.4 gram, II. 0.45 gram, III. 0.45 gram. The escaping gases became inflamed for an instant. The presence of phosphine in the issuing gases was further proved by the silver nitrate test. On addition of the latter reagent to a solution of a part of the liberated gases in water a dark precipitate was found. This precipitate, with the exception of some minute black specks (silver phosphide), redissolved immediately on the addition of ammonia. The black specks redissolved only on vigorous shaking. Some unchanged phosphonium iodide was still to be seen at the lower part of the tube. On further digestion for three hours at 130° to 135° the losses were, I. 0.25 gram, II. 0.25 gram, III. 0.3 gram. The opening of the tubes was accompanied by a sharp noise, the escaping gases burning for a few seconds. The heating was now still further continued for seven hours at 130° to 135° with the result that tube I. lost 0.2 gram, tube II. 0.3 gram, tube III. 0.3 gram of hydrochloric acid and phosphine. The tubes were digested once more, this time for six hours, up to 160°. Only 0.1 gram of gas escaped from each tube, the outflowing gases burning for some time. The reaction was considered as finished. The total losses of the three tubes were, I. 2.65 grams, II. 2.65 grams, III. 2.8 grams.

The reaction-product was removed from the tubes and digested repeatedly with benzene by the aid of a reflux condenser. On concentrating the benzene solution by distillation, a crop of red crystals was obtained which proved to be stannic iodide. This was identified by its melting-point (146° C.) and by analysis.

I. 0.2156 gram substance gave 0.0526 gram SnO_2, corresponding to 0.04138 gram tin.

II. 0.3444 gram substance gave 0.5162 gram AgI, corresponding to 0.2789 gram iodine.

	Calculated for SnI_4.	Found.
Sn	19.01	19.19
I	80.99	80.98

The residue, after extraction with benzene, could be expected to contain stannous chloride, free phosphorus, and perhaps stannous iodide also. Since absolute alcohol is said to dissolve stannous chloride without decomposition while stannous iodide is not known to be soluble in this medium, it was hoped, by treating the residue with absolute alcohol, to separate the stannous chloride. The attempt, however, was a failure. On heating the residue with absolute alcohol a light-red solution was obtained which contained both a chloride and an iodide. The solution soon became much darker in color, and when tested with hydrogen sulphide in the usual way, gave a bright-yellow precipitate, showing, consequently, the presence of a large quantity of a stannic compound. This was perplexing. On concentrating the solution almost all the alcohol had to be evaporated before solidification of the dissolved substance took place. The solid mass was dark-yellow and more or less resinous. It was transferred to a distilling-flask and subjected to a gradually increasing heat. At first some highly-colored alcohol went over; then, upon applying the naked flame directly to the distilling-flask, a slightly-colored, fuming liquid followed, and soon dry, porous, black lumps were seen to form in the distilling-flask. The fuming liquid was tin tetrachloride and the black mass more or less pure tin. It is a well-known characteristic of stannous chloride to break up into stannic chloride and tin.

The following appeared to be shown by the experiments just described: (1) Stannic iodide was present in considerable quantity in the reaction-product, (2) stannous chloride was undoubtedly proved to be a part of the latter, (3) red phosphorus (which remained after the residue obtained upon the removal of the stannic iodide was treated with alcohol) was one of the products of the reaction, and (4) a certain amount of hydrochloric acid and phosphine were evolved. Guided especially by the quantity of gases evolved, the follow-

ing equation appeared to represent the reaction which took place :

$$4SnCl_4 + 4PH_4I = SnI_4 + 3SnCl_2 + 10HCl + 2PH_3 + P_2.$$

According to this equation a loss of 2.7 grams of hydrochloric acid and phosphine would correspond to 4 grams of phosphonium iodide (with its equivalent quantity of tin tetrachloride) while in the three tubes described above there were lost respectively, 2.65 grams, 2.65 grams, and 2.8 grams.

As was discussed above, the strange thing about such a reaction would be that stannic iodide should remain unreduced. In order to clear up this apparent anomaly another series of experiments was carried through.

Two tubes were filled as before with 6.5 grams of tin tetrachloride and 4 grams of phosphonium iodide, but this time no small tube was used to keep the two substances apart. While filling the digestion-tube in this case it was kept surrounded by a mixture of salt and ice, for we had found that at the temperature of a freezing-mixture phosphonium iodide and tin tetrachloride do not act upon one another in the slightest. As a result of this method of filling the tubes, not only is the reaction considerably accelerated owing to the mixing of the substances directly, but the direct mixing is probably necessary for the complete reaction. In the latter period of the digestion the resulting mass is very compact, and thorough mixing, as well as free communication throughout the tube, appears to be a great advantage. The presence of a small tube inside the larger is certainly an impediment in this case.

But even with the freely mixed substances the reaction was slow. After digesting for a long time, during which the tubes were opened from time to time, and the temperature raised toward the end to from 160° to 170°, a total loss of 2.95 grams and 3.05 grams, respectively, was noted. Having kept the tubes for a couple of hours at 160° to 170°, and having observed a loss of only 0.1 gram in each case, the reaction was therefore considered as completed.

The contents of one tube (loss 3.05 grams) was treated repeatedly with carbon disulphide in which tin tetraiodide is

said to be very soluble, but on concentrating the filtrate very little tin tetraiodide was found. It occurred to us that it might be advisable to digest the phosphonium iodide and tin tetrachloride at a still higher temperature. The remaining tube was therefore heated for some hours at 250° to 260°, upon which an additional loss of 0.2 gram was observed (total loss 3.15 grams). In this tube scarcely any tin tetraiodide could be detected, after repeated digestion with benzene under the reflux condenser. Having settled the question as to the absence of tin tetraiodide, it remained only to identify the stannous chloride and iodide. The presence of stannous compounds was demonstrated by tests presently to be described.

The residue, after treatment with benzene, was dried and shaken up with water, from which the air was removed by boiling, and the liquid filtered. The first part of the filtrate, as it came through, appeared to be clear, but soon the whole filtrate became turbid. A portion of the filtrate clarified by a couple of drops of hydrochloric acid, gave the characteristic dark-brown precipitate of stannous sulphide. Another portion of the filtrate, acidified with hydrochloric acid, was added to a solution of mercuric chloride—a cinnabar-red precipitate was formed which, upon further addition of the filtrate and warming, turned into metallic mercury. An ammoniacal solution of silver nitrate was also reduced by the filtrate.

In order to demonstrate that both iodine and chlorine were present in the filtrate a portion of the latter, acidified with tartaric acid, was treated with hydrogen sulphide, the dark-brown precipitate filtered off, and the filtrate heated to drive off the hydrogen sulphide. On addition of silver nitrate to this filtrate a light-yellow precipitate was formed which only partly redissolved in ammonia. On filtering off the precipitate and neutralizing the filtrate with nitric acid, a white precipitate of silver chloride separated.

It appears from the above tests that the presence of stannous chloride and stannous iodide in the reaction-product is unmistakably proved.

If in the products of the reaction between tin tetrachloride

and phosphonium iodide stannic iodide is absent, then the reaction has to be represented by the following equation:

$$6SnCl_4 + 6PH_4I = 3SnCl_2 + 3SnI_2 + 18HCl + 2PH_3 + 4P.$$

Strongly corroborative of this equation is the consideration of the amount of gases set free in the reaction. In the tubes which were digested under the most favorable circumstances the loss of the escaping gases was respectively 3.05 and 3.15 grams. According to this last equation the loss should be 3.3 grams.

The study of the reaction between phosphonium iodide and tin tetrachloride shows that the former is just as effective in reducing the latter as it was in reducing antimonic chloride.

The study seems, moreover, to afford some insight into the successive steps by which the final reduction of tin tetrachloride is gradually accomplished. The formation of stannous iodide results, at least in part, from the reduction of the stannic iodide previously formed.

The action of phosphoretted hydrogen upon stannic chloride was studied by H. Rose[1] and R. Mahn.[2] According to the former, tin tetrachloride absorbs hydrogen phosphide and gives a yellow solid, which fumes in the air. Mahn, by distilling this addition-product in a current of carbon dioxide, got rid of the unchanged tin tetrachloride, to which the fuming was due, and obtained a non-fuming, dark powder. A series of discordant analyses of this powder led him to the formula $Sn_3Cl_6P_3$.

Contributions from the Chemical Laboratory of Union College.

CERTAIN SUBSTITUTION DERIVATIVES OF ETHYL ANILINOMALONATE.

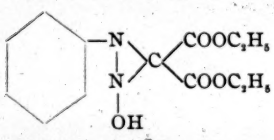
By Richard Sydney Curtiss.

In two previous papers[3] I described a compound produced by the action of nitrous acid on ethyl anilinomalonate,

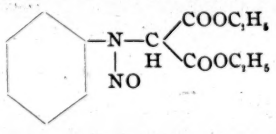
$$C_6H_5NH.CH(CO_2C_2H_5)_2.$$

[1] Pogg. Ann., **24**, 159.
[2] Jenaische Ztschr. f. Medicin u. Naturwiss., **5**, 158.
[3] This Journal, **23**, 509; **28**, 315.

Sodium and potassium hydroxides react with this compound to form well-defined salts. It gives Liebermann's nitroso reaction (contrary to a former erroneous statement),[1] while its alcoholic solution reacts but slowly with ferric chloride, producing a dull-red color. The substance is either ethyl phenyloxydiazomalonate[2] (I.) or ethyl nitrosoanilinomalonate (II.), or perhaps a mixture of the two tautomeric compounds:



I.



II.

As the substance decomposes easily when brought into contact with reagents, and gives nitrogen and its oxides, the corresponding ortho-, meta-, and para-substituted methyl derivatives have been made, with the idea that some of these might have a greater stability of the nitrogen chain, thereby rendering more easy the study of their structure as acids, or pseudo-acids.

In order to prepare these compounds it was first necessary to make the ortho-, meta-, and paratoluidinomalonates. These were formed from ethyl brommalonate (b. p. 120° to 125° under 14 mm. pressure) and Kahlbaum's pure toluidines, by the general method already given[3] for making ethyl anilinomalonate.

The ethyl ortho-, meta-, and paratoluidinomalonates are weak bases. Their salts with the strong mineral acids are decomposed by water, the base usually separating in the form of an oil. When treated with nitrous acid they yield thick, amber-colored oils. When treated with sodium or potassium hydroxides these amber oils give yellow solutions, or stable, yellow, crystalline salts. They also give Liebermann's nitrosamine test, and react slowly with ferric chloride solution, forming deep-red colors.

[1] This JOURNAL, **23**, 510.

[2] *Ibid.*, **28**, 315. Incorrectly printed as ethyl α-phenyloxydiazomalonate.

[3] *Ibid.*, **19**, 693.

In describing the compounds formed by the action of nitrous acids on these bases, they will, for convenience, be spoken of at present as nitrosamines. Their possible tautomeric structure, as substituted ethyl phenyloxydiazomalonates (I.) will be considered in a later paper on this subject.

EXPERIMENTAL PART.

Ethyl Orthotoluidinomalonate,

.—

To prepare this substance 50 grams of ethyl brommalonate (1 molecule) are mixed with 60 grams of orthotoluidine ($2\frac{2}{3}$ molecules). If the mixture is allowed to stand several days it gradually darkens and a crystalline mass separates. It is better, however, to heat it on the water-bath at 100°. This causes the clear liquid to darken and the separation of orthotoluidine hydrobromide begins in a few minutes. The reaction is complete in one or two hours.

The crystal mass is filtered and washed with ether, with the aid of a pump. The magenta-colored filtrate is then washed with a slight excess of dilute hydrochloric acid, to remove the unchanged base, as well as the colored impurities. The ethereal solution, when dried over calcium chloride and the ether distilled off, leaves a clear, reddish-yellow oil (the yield is 92 per cent of the theory). This product was freed from ethyl brommalonate and other impurities, by treatment with hydrochloric acid gas, as described below. This forms a salt with the base. To regenerate the base from the purified hydrochloride it is only necessary to shake the latter with water and ether. The ethereal solution is then thoroughly washed with water to neutral reaction and dried over calcium chloride. When the ether is distilled off in a vacuum a nearly colorless oil is left which slowly reddens on standing several days in the light. The base thus purified and dried over sulphuric acid was used in the following analysis :

0.2630 gram substance gave 0.6094 gram CO_2 and 0.1726 gram H_2O.

0.2743 gram substance gave 12.9 cc. N at 14° and 750.3 mm.

	Calculated for $CH_3.C_6H_4.NH.CH(CO_2C_2H_5)_2$.	Found.
C	63.33	63.16
H	7.22	7.34
N	5.30	5.51

It is easily soluble in benzene, acetone, chloroform, ether, alcohol, and ligroin. It slowly reduces an ammoniacal silver nitrate solution, forming a bright mirror, and an alkaline solution of potassium permanganate is instantly decolorized. It dissolves in concentrated hydrochloric and sulphuric acids, and is reprecipitated from these solutions by adding an equal volume of water. Concentrated nitric acid forms with it, on standing, a yellow, crystalline product, soluble in ether and insoluble in water. When the oil is heated to the point of distillation, decomposition is effected, gases are evolved, and on cooling a light-green, crystalline compound appears, which melts at about 140°, and is soluble in a solution of sodium hydroxide. This change will be further studied.

Ethyl Orthotoluidinomalonate Hydrochloride.—A solution is made of the above-mentioned base, in an equal volume of ether, and dry hydrochloric acid gas is passed into it until the reaction is complete. The resulting dark-red solution may be quickly changed to a crystalline mass by rubbing with a glass rod. Inasmuch as this salt, even when pure, fumes in the open air, and is rapidly decomposed by moisture, it is best purified when washed with dry toluene by decantation, rather than on the filter.

The salt, when dried in a vacuum over sulphuric acid, was analyzed.

0.3018 gram substance gave 0.1440 gram AgCl.

	Calculated for $CH_3.C_6H_4.NH(HCl).CH(CO_2C_2H_5)_2$.	Found.
Cl	11.76	11.80

Prepared as above, it is a white, or pink-white, crystalline substance, which melts at 87° to 90°. It may be kept in the

dark over sulphuric acid for months, but when exposed to light it quickly turns to a magenta color. It dissolves readily in acetone and chloroform, is fairly soluble in alcohol, and slightly so in ether, toluene, benzene, and carbon tetrachloride, and is easily decomposed by water into hydrochloric acid and the original base, as stated above.

Ethyl Nitrosoorthotoluidinomalonate.—This substance may be made either from the free base in acid solution, or from the hydrochloride itself, prepared as above.

Forty and one-tenth grams of the hydrochloride are mixed with 50 cc. of water, which liberates the base as an oil. To this 9.5 grams of pure sodium nitrite (0.3 gram excess) dissolved in 25 cc. of water, are slowly added. The mixture is constantly shaken in a well-stoppered bottle and kept below 15°. The absorption of nitrous acid is complete and the operation is finished in twenty minutes. After the bottle containing the oily emulsion has stood in cold water three-quarters of an hour, the mixture is extracted with ether. The latter is washed thoroughly, first with cold water, then with a little sodium carbonate solution, and lastly, many times with cold water. This golden-yellow ethereal solution, dried over calcium chloride and evaporated in a vacuum, leaves 37.5 grams of an oil. This could neither be crystallized nor distilled. The substance yields well-defined alkali salts,[1] and for its purification it was regenerated from one of these.

Regeneration of Ethyl Nitrosoorthotoluidinomalonate from its Sodium Salt.—Five grams of the pure, finely-powdered salt are partly dissolved in 25 cc. of cold water, and to this 25 cc. of ether are added. A rapid stream of carbon dioxide is passed through the liquids, which are kept cold by immersing the flask in ice-water. The yellow color of the aqueous solution gradually passes into the colorless ether as the decomposition goes on. In twenty to thirty minutes, when the water has become colorless, which fact indicates the end of the reaction, the ether is separated and washed with cold water to neutral reaction. It is then dried over calcium chloride.

[1] The preparation and properties of these alkali salts will be described in a later paper.

While evaporating the ether off in a vacuum-desiccator, light-colored crystals formed in small quantity on the sides of the cold dish. These soon melted at the temperature of the room, and could not be obtained again even when the oil stood for a long time at a very low temperature. The above product is a clear oil of a slight reddish tint, has the consistency of honey, is nearly odorless, and could not be crystallized. It undergoes no change on being kept in a desiccator, over sulphuric acid, for six weeks. The yield is 3.8 grams. It was dried over sulphuric acid for five or six days and analyzed.

0.3023 gram substance gave 0.6299 gram CO_2 and 0.1697 gram H_2O.

0.2061 gram substance gave 17.2 cc. N at 15° and 754.5 mm. pressure.

	Calculated for $CH_3.C_6H_4.N.(NO).CH.(CO_2C_2H_5)_2$.	Found.
C	57.08	56.79
H	6.17	6.28
N	9.55	9.80

The substance thus purified gives the Liebermann nitroso reaction. Its alcoholic solution is changed by ferric chloride to a dull-red color, which does not appear immediately, however, but becomes faintly apparent only after three or four seconds have elapsed, and then darkens slowly. It dissolves easily in chloroform, carbon tetrachloride, benzene, acetone, and ethyl acetate, is fairly soluble in alcohol and ether, and slightly so in ligroin. It is insoluble in cold water, but dissolves sparingly in hot. A solution of sodium carbonate dissolves it slightly and assumes a yellow color. Concentrated solutions of sodium and potassium hydroxides form immediate precipitates of well-crystallized salts, from which the original oil may be regenerated by mineral acids, or even by carbonic acid, as described above.

Ethyl Metatoluidinomalonate.—Twenty-four grams of ethyl brommalonate were mixed with 21.4 grams of metatoluidine (about 3 molecules). After standing at ordinary temperatures for two hours, crystals of toluidine hydrobromide begin to separate. The reaction is hastened by heating the mixture

from forty to sixty minutes at 100°, on the water-bath. This completes the reaction, and causes the crystalline mass to turn green if longer continued. After cooling, the dissolved hydrochloride is precipitated from the thick, dark liquid by the addition of three or four volumes of ether, and is then filtered off on the pump. The yield is 85 to 95 per cent of the theory.

The red, ethereal solution is then worked up as described above, in the preparation of ethyl orthotoluidinomalonate. When it is brought to that stage of the process, where the ether is evaporated, the new compound slowly crystallizes out as a dark mass of rosettes of prismatic needles. This is then freed from the oily mother-liquor by suction with a filter-pump, and washed thoroughly with ligroin. The product is 21 grams of lavender-white crystals. This is purified for analysis by recrystallization from ligroin or absolute alcohol. Thus prepared, it forms colorless needles. It melts at 50°.5 to 51°, forming a clear liquid which does not change when heated to 200°. From 220° to 250° gases are given off, and, after cooling, a new crystalline mass appears. This product will also be further studied.

The analysis of the pure base (m. p. 50°.5 to 51°) follows:

0.2070 gram substance gave 0.4819 gram CO_2 and 0.1331 gram H_2O.

0.3206 gram substance gave 15.2 cc. N at 16°.5 and 732.1 mm.

	Calculated for $CH_3.C_6H_4.NH.CH(CO_2C_2H_5)_2$.	Found.
C	63.33	63.45
H	7.22	7.19
N	5.30	5.37

The substance dissolves easily in ether, chloroform, acetone, toluene, and benzene, is slightly soluble in alcohol, dissolves very easily in hot ligroin, but is nearly insoluble in the cold solvent. Concentrated hydrochloric acid dissolves it, but it is reprecipitated as an oil on the addition of much water to this solution. It rapidly reduces an alkaline solution of potassium permanganate. Ammoniacal silver nitrate is reduced slowly, forming a dark deposit of silver.

Ethyl Metatoluidinomalonate Hydrochloride.—When dry hydrochloric acid gas is passed, to saturation, through an ethereal solution of ethyl metatoluidinomalonate, and the ether and excess of acid are evaporated over sulphuric acid, a thick, colorless oil is left. By rubbing this with a little ligroin, at a low temperature, the oil is with difficulty made to crystallize. After a crystal has been once obtained, however, and a minute particle is thrown into the oil, it solidifies quickly. This crystalline mass was washed entirely by decantation, first with dry ligroin, then with ligroin-benzene, and allowed to stand in a vacuum over sulphuric acid for two or three weeks. It was then analyzed:

0.4040 gram salt gave 0.1871 gram AgCl.

	Calculated for $CH_3.C_6H_4.NH(HCl).CH(CO_2C_2H_5)_2$.	Found.
Cl	11.76	11.45

The salt crystallizes from its solutions in alcohol or ether in beautiful rosettes of white, silky needles. It is easily soluble in chloroform, benzene, acetone, ethyl acetate, and alcohol; fairly so in ether and toluene; slightly so in carbon tetrachloride and ligroin. It melts at 80° to 83°, forming a clear liquid.

Ethyl Nitrosometatoluidinomalonate.—This substance can best be prepared according to the following method: 13.3 grams of the pure crystals of ethyl metatoluidinomalonate are finely pulverized and mixed with 2.5 grams (0.1 gram excess) of real sulphuric acid in 27 cc. of water. To this 3.9 grams (0.4 gram excess) of pure sodium nitrite, in 40 cc. of water, are slowly added with constant shaking. The temperature of the mixture should be kept below 15°. The reaction begins immediately. The white powder in suspension in the water at first turns yellow, then soon becomes packed into an oily ball. To increase the surface exposed to action a little ether is added which dissolves both the amine and its reaction-product. The agitation of the mixture is continued for ten to fifteen minutes after the addition of the nitrite is complete. The ether is then separated from the yellow aqueous solution and washed once with water, then with a solution of sodium

carbonate to alkaline reaction, and finally very thoroughly with cold water. This ethereal solution, after being dried over calcium chloride, is evaporated down on the water-bath, the last portions of ether being removed in a vacuum-desiccator over sulphuric acid. During this process crystals separate out. The dry crystalline mass is washed with ether with the aid of a filter-pump. The filtrate is colored a deep strawberry-red, while the crystals themselves have a faint reddish-yellow color. The yield was 9.1 grams.

From the mother-liquor and washings, 3.4 grams more of deep-red crystals were obtained. The total yield was nearly quantitative. The substance is best purified by recrystallization from hot ligroin (b. p. 60° to 80°). On cooling a hot saturated solution it separates, at first, as an oil. However, by slow and careful cooling, while rubbing with a glass rod, it can be made to separate in a pure crystalline form. This product, filtered and well washed with cold ligroin, dried in a vacuum over sulphuric acid, and analyzed, gave the following figures:

0.2229 gram substance gave 0.4652 gram CO_2 and 0.1244 gram H_2O.

0.1986 gram substance gave 16.4 cc. N at 19°.2 and 755.4 mm.

	Calculated for $CH_3.C_6H_4.N.(NO).CH(CO_2C_2H_5)_2$.	Found.
C	57.08	56.89
H	6.17	6.24
N	9.55	9.56

Thus purified the substance consists of beautiful, transparent, pinkish-amber prisms[1] (apparently monoclinic), which melt at 58° to 58°.5, forming a clear liquid. If the heating be continued above its melting-point, gases are evolved from 125° to 200°. At 220° the color darkens. If cooled at this point a crystalline body is obtained, which melts at 126° to 127°. This new substance is fairly soluble in alcohol and in ether and does not give the nitrosamine test of Liebermann.

[1] The pink color is no doubt due to very slight traces of a decomposition-product which cannot be completely removed by repeated recrystallization, inasmuch as attempts to decolorize it, by boiling its alcoholic solution with pure bone-black, resulted in the formation of larger quantities of this brilliant orange-red impurity.

Ethyl nitrosometatoluidinomalonate becomes highly electrified on rubbing with a glass rod. It dissolves readily in benzene, toluene, xylene, ethyl acetate, acetone, and glacial acetic acid; is fairly soluble in ether and alcohol; only slightly so in cold ligroin, but dissolves easily when the ligroin is hot. Cold solutions of sodium carbonate and sodium hydroxide act slowly on the body, as it is insoluble in water. If, however, these solutions are warmed to the melting-point of the crystals it dissolves fairly well. On neutralizing the resulting yellow solutions with dilute hydrochloric acid the nitrosamine is regenerated and appears as a white, oily emulsion.

The crystalline body gives Liebermann's nitrosamine test. Ferric chloride added to a dilute alcoholic solution of the crystals, turns it, at first, straw-yellow, then, after a few seconds, it begins to redden and gradually assumes a dark, brownish-red color in thirty to sixty seconds.

Ethyl Paratoluidinomalonate.—This compound has already been described briefly by Blank,[1] and has the solubilities ascribed to it by him. I have made it in large quantities by the general method described above in making the analogous bases, and note here the following additional properties.

It is a weak base like the ortho- and meta-isomers. It dissolves in concentrated hydrochloric and sulphuric acids and is reprecipitated, by addition of water, as an oil which soon crystallizes. Cold nitric acid, acting on it, appears to form a yellow compound soluble in ether.

Its alcoholic solution slowly reduces a hot, ammoniacal, silver nitrate solution to metallic silver, and an alkaline solution of potassium permanganate is instantly decolorized by it.

The behavior of these substituted ethyl anilinomalonates with weak oxidizing agents is of interest, inasmuch as it has been shown[2] that ethylanilinomalonate itself, simply by being oxidized with mercuric oxide or potassium permanganate, in ligroin solution, undergoes a peculiar reaction, by which it is changed to ethyl dianilinomalonate.

[1] Ber. d. chem. Ges., 31, 1815.

[2] Curtiss: This JOURNAL, 19, 694.

It is of interest to note, however, that recent experiments have shown that no such transformation results if a little calcium chloride powder is added to the ligroin solution to hold the water which may be formed by the oxidation of the two very reactive hydrogen atoms (1 and 2).

Ethyl Nitrosoparatoluidinomalonate.—To make this compound, 4.7 grams of finely powdered ethyl paratoluidinomalonate are dissolved in a little ether and mixed with 0.95 gram of sulphuric acid in 20 cc. of water. To this, in a well-stoppered bottle, is slowly added a solution of 1.3 grams of pure sodium nitrite in 20 cc. of water. The reaction proceeds under the same general conditions as already described in similar cases, and is complete in thirty to forty minutes. After washing the ethereal solution well with a solution of sodium carbonate, and with water, drying it over calcium chloride, and removing the ether in a vacuum, a clear amber oil remains.

It is purified by regenerating it from its pure sodium salt by means of carbon dioxide, as described above in the purification of ethyl nitrosoorthotoluidinomalonate. It was prepared in this way, dried over sulphuric acid, and analyzed:

0.2986 gram substance gave 0.6230 gram CO_2 and 0.1645 gram H_2O.

0.2719 gram substance gave 22.2 cc. of N at 15° and 746 mm.

	Calculated for $CH_3.C_6H_4.N.(NO).CH(CO_2C_2H_5)_2$.	Found.
C	57.08	56.87
H	6.17	6.16
N	9.55	9.48

The substance is a clear, greenish-yellow oil of honey-like consistency, which gradually turns slightly red while standing two or three weeks in the desiccator over sulphuric acid. It could be obtained in the crystal form only with the greatest

difficulty. On allowing a bit of the oil, in a little ligroin, to stand for a long time at —15°, with occasional rubbing with a glass rod, a few minute crystals were obtained. When one of these was placed in the main lot of oil and left for twenty-four hours at —15°, the latter slowly and only partially crystallized in short, monoclinic prisms. These were mostly lost in attempting to wash them free of the oily mother-liquor, as they are very soluble in all of the ordinary organic solvents. The few crystals remaining gradually liquefied with slight decomposition on standing ten days in the desiccator. The oil, as soon as obtained from its sodium salt, gives the Liebermann nitroso reaction. A ferric chloride solution acting on its alcoholic solution produces no immediate color, but after two or three seconds a faint red color appears, which gradually grows darker for twenty or thirty seconds. It is soluble in solutions of sodium and potassium hydroxide, and if the latter are concentrated, crystalline yellow salts are immediately precipitated.

The oil dissolves easily in ligroin, benzene, toluene, ether, chloroform, alcohol, and ethyl acetate, and is fairly soluble in carbon tetrachloride. It is insoluble in cold water.

The study of these compounds will be continued, and with special reference to the salt-forming properties and general behavior as acids, or pseudo acids, of those described here under the name of nitrosamines.

In closing I wish to express my thanks to Mr. Thomas G. Delbridge, instructor in this laboratory, to whom I am indebted for the above series of carefully conducted combustions.

UNION COLLEGE, SCHENECTADY, N. Y.,
March 16, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CVI.—ON THE DOUBLE AND TRIPLE THIOCYANATES OF CAESIUM, CADMIUM, AND SILVER.

BY H. L. WELLS.

The compounds to be described are as follows :

Double Salts.

$CsCd(SCN)_3$;
$Cs_4Cd(SCN)_6.2H_2O$;
$CdAg_2(SCN)_4.2H_2O$.

Triple Salts.

$Cs_3CdAg_2(SCN)_6.2H_2O$;
$Cs_2CdAg_2(SCN)_6$;
$Cs_2CdAg_4(SCN)_8.2H_2O$;
$Cs_4Cd_3Ag_{10}(SCN)_{20}.6H_2O$.

To make a complete list of the compounds formed by the three simple salts under consideration, the following caesium-silver thiocyanates which have been described previously[1] should be mentioned:

$Cs_3Ag(SCN)_4$;
$Cs_2Ag(SCN)_3$;
and $CsAg(SCN)_2$.

The compound $CsCd(SCN)_3$ corresponds to $CsHg(SCN)_3$, as might be expected from the somewhat close relation of cadmium and mercuric compounds in general, but it is noticeable that there is no caesium-cadmium thiocyanate analogous to $Cs_2Hg(SCN)_4.H_2O$ or $Cs_2Zn(SCN)_4.2H_2O$, the latter being the only caesium-zinc salt which could be prepared.

The salt $Cs_4Cd(SCN)_6.2H_2O$ is rather remarkable from the fact that there is no mercuric or zinc double thiocyanate corresponding to it. It agrees, however, with $Cs_4Mn(SCN)_6$, except that it contains water. These 4 : 1 thiocyanates (leaving water out of consideration) belong to a type which is well-known among the double halides, as is shown by the following list, in which the cadmium salts are prominent:

$(NH_4)_4ZnCl_6$;
$(NH_4)_4CdCl_6$;
$(NH_4)_4CdBr_6$;
K_4CdCl_6;
K_4CdBr_6;
Cs_4PbCl_6;
Cs_4PbBr_6;
$(NH_4)_4SnCl_6.3H_2O$;
$K_4SnCl_6.3H_2O$.

[1] This JOURNAL, 28, 263.

The salt $CdAg_2(SCN)_4.H_2O$ differs from $ZnAg_2(SCN)_4$ in containing a molecule of water of crystallization.

The triple salts $Cs_2CdAg_2(SCN)_6$ and $Cs_2CdAg_2(SCN)_6.2H_2O$ might be regarded as possibly derived from the double salt $Cs_4Cd(SCN)_6.2H_2O$, but it must be borne in mind that there is no apparent connection between most of the other types of triple thiocyanates[1] and the known double salts. The hydrous triple salt just mentioned belongs to the most extensive series of triple thiocyanates which has as yet been prepared. A list of them follows:

$Cs_2CaAg_2(SCN)_6.2H_2O$;
$Cs_2MgAg_2(SCN)_6.2H_2O$;
$Cs_2MnAg_2(SCN)_6.2H_2O$;
$Cs_2NiAg_2(SCN)_6.2H_2O$;
$Cs_2NiCu_2(SCN)_6.2H_2O$;
$Cs_2CoAg_2(SCN)_6.2H_2O$;
and $Cs_2CdAg_2(SCN)_6.2H_2O$.

The anhydrous triple salt $Cs_2CdAg_2(SCN)_6$, which is much more readily formed than the corresponding hydrous compound, is interesting, since it shows that water of crystallization is not essential to this general type of triple salts. It is evident, therefore, that water may be left out of consideration, in this case at least, in comparing the different types of these salts. This argument strengthens the view advanced in the previous communication,[2] that water does not appear to replace other constituents in passing from one type to another of triple thiocyanates.

The triple salts

$Cs_2CdAg_4(SCN)_8.2H_2O$ and $Cs_4Cd_3Ag_{10}(SCN)_{20}.6H_2O$

represent new types. These two salts are not far apart in chemical composition, but they show distinct crystalline forms, as far as one habit of the first salt is concerned, but this has another habit of crystallization which closely resembles the second salt. A careful consideration of the analyses shows that the second salt, which is formed in the

[1] This JOURNAL, 28, 245.
[2] *Ibid.*, 28, 254.

presence of an excess of cadmium thiocyanate, does not differ from the first salt simply in containing more cadmium thiocyanate, for the ratios of Ag to SCN are very close to 1 : 2 in both products, a condition which would be modified by simply varying cadmium thiocyanate. It seems possible, perhaps, that the salt with the complicated formula may be due to the crystallization of the first salt, $Cs_2CdAg_4(SCN)_8.2H_2O$, with an undiscovered, isomorphous salt, $CsCdAg_3(SCN)_5.2H_2O$. It will be seen in the experimental part that a slight indication of the existence of the latter compound has been obtained. If it does exist, it is also a new type.

The entire lack of agreement between the triple thiocyanates of cadmium and those of zinc is very remarkable in view of the resemblance of many compounds of these two metals. This unexpected lack of correspondence appears to be in harmony with the disagreement of the double thiocyanates which has already been pointed out. For the sake of comparison, the formulas of the triple salts containing zinc and cadmium are here placed side by side :

$CsZnAg(SCN)_4.H_2O$;	
$Cs_2ZnAg(SCN)_5$;	
	$Cs_2CdAg_2(SCN)_6$;
	$Cs_2CdAg_2(SCN)_6.2H_2O$;
$CsZn_2Ag_3(SCN)_8$;	
$CsZn_2Ag_4(SCN)_9$;	
	$Cs_2CdAg_4(SCN)_8.2H_2O$;
	$Cs_4Cd_3Ag_{10}(SCN)_{20}.6H_2O$.

There are eight types of triple thiocyanates in the above table, and all but one of the salts are unique in their types. The two other types known at present are represented by four salts corresponding to $Cs_2BaAg_2(SCN)_6$, and the single salt $K_4BaAg_2(SCN)_8.H_2O$.

EXPERIMENTAL PART.

The cadmium thiocyanate used for this work was prepared by making an exact precipitation with barium thiocyanate and cadmium sulphate in dilute solution, filtering, and evapo-

rating to crystallization. The salt is sparingly soluble and crystallizes without water, as stated by Meitzendorff.[1]

1 : 1 Caesium-Cadmium Thiocyanate, $CsCd(SCN)_3$.—This salt forms large crystals which are sometimes tabular, and again prismatic in habit. They are colorless and either transparent or frequently somewhat white and not fully transparent. The substance is stable in the air. It melts at 212° to 214°. The compound is formed under a wide range of conditions, for instance, when caesium and cadmium thiocyanates are mixed in the molecular proportions 8 : 1, 1 : 1, and 1 : 4 in aqueous solution and properly concentrated. In the case of the first proportion mentioned, the solution should not be concentrated too far, for then the 4 : 1 salt, to be described next, would be deposited. The volume should be about 100 cc. for 75 grams of caesium thiocyanate and 12 grams of cadmium thiocyanate. When 4 molecules of cadmium thiocyanate to 1 of the caesium salt are present in a solution, cadmium thiocyanate is usually deposited with the double salt. The salt can be recrystallized from water.

The following analyses were made of different crops:

	Calculated for $CsCd(SCN)_3$	Found. I.	II.	III.	IV.	V.
Cs	31.71	....	....	....	....	....
Cd	26.80	26.85	26.80	....	....	27.46
SCN	41.49	41.10	41.59	41.41	41.19	41.91

4 : 1 Caesium-Cadmium Thiocyanate, $Cs_4Cd(SCN)_6.2H_2O$.—This salt forms large, nearly square, tabular crystals which are transparent, colorless, and stable in the air. It fuses gradually from 80° to 90°, gives off water, and the anhydrous residue fuses between 110° and 120°. It is formed in concentrated solutions, best when they contain more than the calculated amount of caesium thiocyanate, and when the excess of the latter is very large it crystallizes beside the double salt. By cooling a very concentrated solution of the salt it is possible to recrystallize it, but the 1 : 1 salt is deposited if the solution is more dilute.

The following analyses of different crops were made:

[1] Pogg. Ann., 86, 63.

	Calculated for $Cs_4Cd(SCN)_6.2H_2O$.	Found. I.	II.	III.	IV.
Cs	51.73	....	....	....	....
Cd	10.93	10.66	....	....	....
SCN	33.84	33.59	33.65	33.67	33.88
H_2O	3.50	3.27	....	....	....

Anhydrous, 2 : 1 : 2, Caesium-Cadmium-Silver Thiocyanate, $Cs_2CdAg_2(SCN)_6$.—This salt is deposited on cooling and standing from solutions of almost any mixture of the three salts unless they are very dilute. When it forms rapidly it produces an exceedingly finely divided, snow-white precipitate. When it deposits more slowly it usually forms small, compact, spherical, white concretions in which the individual crystals are difficult to detect, even with a microscope of high power. In rather concentrated solutions, however, particularly those containing a very large excess of caesium thiocyanate, it is possible to obtain the compound in the form of groups of brilliant, thin scales, which are sometimes several millimeters in diameter. The best crystallized crops were obtained from a solution containing about 150 grams of caesium thiocyanate, 10 grams of cadmium thiocyanate, and 5 grams of silver thiocyanate at volumes varying from 250 to 300 cc. The readiness with which this compound is formed is a great obstacle to the preparation of the hydrous salt corresponding to it.

Analyses were made of several crops. No. I. was in the form of small spherical masses, No. II. was a precipitate, Nos. III., IV., and V. were in the form of small scales:

	Calculated for $Cs_2CdAg_2(SCN)_6$.	Found. I.	II.	III.	IV.	V.
Cs	28.23	....	....	....	....	....
Cd	11.92	12.92	11.95	....	....	....
AgSCN	35.23	34.99	34.01	....	....	....
Sol. SCN	24.62	24.84	23.46	25.03	25.04	24.46

Hydrous, 2 : 1 : 2, Caesium-Cadmium-Silver Thiocyanate, $Cs_2CdAg_2(SCN)_6.2H_2O$.—This salt forms transparent, prismatic crystals. Usually the crystals form groups, radiating from common points, with the individuals a centimeter or more in length and about a millimeter in diameter, but sometimes loose masses are formed when the individual crystals

are often exceedingly small and slender. The salt was observed under a wide range of conditions, but it does not appear to be formed readily in solutions containing a great excess of cadmium thiocyanate. It is extremely difficult to obtain pure crops of this compound, because the anhydrous salt is almost invariably deposited with it or upon it. It is probably best to use caesium and cadmium thiocyanates in nearly the required proportion with comparatively little of the silver salt. Then, at a certain degree of dilution, the salt will be deposited after cooling, and, on rare occasions, it may be obtained free from the white concretions of the anhydrous salt. The salt loses water very quickly on exposure to the air, becoming white and opaque.

Water was determined in a sample of the transparent crystals with the following result:

	Calculated for $Cs_2CdAg_2(SCN)_6.2H_2O$.	Found.
H_2O	3.68	4.22

Three samples, made under widely varying conditions, were analyzed after they had lost water by exposure or by drying at 100°, with the following results:

	Calculated for $Cs_2CdAg_2(SCN)_6$.	Found. I.	II.	III.
Cs	28.23	....	....	....
Cd	11.92	12.25	....	....
AgSCN	35.23	34.81	34.98	35.14
Sol. SCN	24.62	24.96	24.95	24.66

2 : 1 : 4, Caesium-Cadmium-Silver Thiocyanate, $Cs_2CdAg_4(SCN)_8.2H_2O$.—This salt is deposited from very dilute solutions which contain a moderate or large excess of caesium thiocyanate in comparison with the cadmium thiocyanate present, and also from very dilute solutions containing the two salts in nearly equal quantities. When the cadmium salt is considerably in excess the salt

$$Cs_4Cd_3Ag_{10}(SCN)_{20}.6H_2O$$

appears to be the invariable product under otherwise similar conditions. The salt is deposited either by cooling or upon long standing, sometimes only after many days, as a solution

evaporates spontaneously. The solutions from which it forms are so dilute that they can hold but little silver thiocyanate in solution, and the crops obtained, even with 1000 or 1200 cc. of solution, are so small that it is difficult to obtain enough for satisfactory analyses. The compound has been observed in three different habits: (1) Minute needles, 2 or 3 mm. in length, mostly in groups of a few individuals radiating from points. Under the microscope these crystals were made out to be hexagonal prisms with pyramids. Professor Penfield has kindly confirmed this observation, and upon comparing these needles with crystals of the 4 : 3 : 10 salt, to be described next in order, he was unable to perceive any relationship between the two kinds of crystals (Analysis I.). (2) Small, thin, diamond-shaped crystals formed slowly (Analysis II.). The crystals of this crop resembled strongly those of the next salt to be described. Professor Penfield, who kindly compared the two kinds of crystals, found them to have similar optical properties, and he thought that they were identical. The analyses show much difference, however. (3) Still smaller and thinner scales, of undetermined shape, formed rapidly by cooling from two very different solutions (Analyses III. and IV.).

The analyses follow:

	Calculated for $Cs_2CdAg_4(SCN)_8.2H_2O$.	Found. I.	II.	III.	IV.
Cs	20.30	....	20.10	....	....
Cd	8.58	8.93	8.65	8.35	8.76
AgSCN	50.67	51.07	50.56	50.43	50.84
Sol. SCN	17.70	17.89	....	17.73	17.80
H_2O	2.75	3.12	....	....	....

4 : 3 : 10, Caesium-Cadmium-Silver Thiocyanate, $Cs_4Cd_3Ag_{10}(SCN)_{30}.6H_2O$.—This occurs in brilliant, colorless, or faint-yellowish crystals, sometimes 2 or 3 mm. in diameter, but usually smaller. The crystals appear to be orthorhombic in form, and are almost invariably of diamond-shaped (rhombic) outline, resulting from prominent faces forming rather low, elongated pyramids. The salt is deposited from dilute solutions containing greater quantities of cadmium

thiocyanate than of the caesium salt, which are nearly saturated with silver thiocyanate, best by evaporation at ordinary temperatures. The crystals often form at the surface of the liquid, but they form also at the bottom. From the less dilute solutions the compound is frequently deposited together with the white spherules of $Cs_2CdAg_2(SCN)_6$, but it is formed alone when such solutions are sufficiently diluted. Many crops were prepared and analyzed, on account of the complex composition indicated. These crops came from two solutions, one of which contained a much greater excess of cadmium thiocyanate than the other, and during the progress of the experiments this excess was still further increased. Both solutions were gradually diluted, and the analyses are given in the order in which they were made, so that the analyses with higher numbers generally represent products from more dilute solutions than the preceding ones. The dilutions were carried to a point where but little silver thiocyanate could be dissolved in the solutions at about 1200 cc. (a portion of the liquid being removed at each step), and the crops of triple salt became too small for satisfactory analyses.

The analyses, all of which represent separate products, are given in the table on the opposite page.

It is to be observed that the crops from the more dilute solutions show a slight tendency to approach the composition represented by the simpler formula, but since all the crops were formed in the presence of an excess of cadmium thiocyanate, a deficiency in cadmium would not be expected in them, and hence the more complex formula has been reluctantly adopted.

Methods of Analysis.—In analyzing the salts described in this article, a substance containing silver was treated with a liberal amount of water, usually at boiling, for some time, then the silver thiocyanate was collected on a Gooch filter, dried at somewhat above 100°, and weighed. Cadmium was sometimes precipitated as sulphide, which was also weighed in a Gooch crucible. This was always the case where caesium was to be determined by weighing the normal sulphate. Cadmium was determined in other cases by precipitation with

	Calculated for $Cs_4CdAg_{10}(SCN)_{20}.6H_2O$.	Found.									Calculated for $CsCdAg_2(SCN)_6.2H_2O$
		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	
Cs	16.54	....	....	16.38	....	....	16.58	15.97	15.91	....	....	13.95
Cd	10.48	9.99	....	10.26	10.26	10.47	10.70	10.48	10.46	10.40	10.98	11.79
AgSCN	51.60	51.74	51.57	51.91	51.95	51.18	51.60	52.04	51.96	52.04	52.05	52.23
Sol. SCN	18.03	18.36	18.26	....	18.08	18.25	....	....	....	....	....	18.25
H_2O	3.35	....	3.31	3.28	3.38	3.23	3.40	....	....	....	....	3.78

sodium carbonate and weighing the oxide in a Gooch crucible. This method frequently gave some trouble, as the carbonate was finely divided and difficult to filter, but in these cases the operation was repeated until the filtrate was clear. The filtrate from the cadmium carbonate was frequently titrated for soluble SCN, but sometimes a separate sample was used for this purpose. Water was determined by loss upon heating to constant weight, usually at about 120°.

NEW HAVEN, CONN., April, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CVII.—ON A DOUBLE SALT OF POTASSIUM AND BARIUM NITRATES.

BY WM. K. WALLBRIDGE.

The salt to be described, $2KNO_3.Ba(NO_3)_2$, is of considerable interest, because other double salts of alkali metals and barium are apparently entirely unknown, and because, while a few double nitrates are known, no evidence has been obtained previously that alkaline nitrates form crystallizable double nitrates with the nitrates of bivalent metals.[1] For these two reasons, therefore, the salt is a very unusual one, and one whose existence would not be expected from analogy.

When a hot, concentrated solution of 40 grams of potassium nitrate and 10 grams of barium nitrate was allowed to cool, large crystals of potassium nitrate formed, and afterwards a crop of small, opaque crystals was deposited upon them. These were carefully picked out and dried by pressing with filter-paper (Analysis I.). On evaporation of the mother-liquor a similar crop was deposited upon potassium nitrate crystals (Analysis II.). The double salt, free from crystals of potassium nitrate, was then obtained from a solution of 40 grams of potassium nitrate and 20 grams of barium nitrate (Analysis III.). From a solution of 20 grams each of the two nitrates a crop was obtained which contained a much larger amount of barium than the double salt. This was evidently a mixture of the double salt with barium nitrate, but it was the only crop analyzed which indicated a mixture. From the

[1] See Wells, Beardsley, and Jamieson: This JOURNAL, 26, 275.

mother-liquor from this mixture a crop of the double salt was obtained (Analysis IV.). Another crop was prepared by slow evaporation, over sulphuric acid, of a solution containing 40 grams of potassium nitrate and 20 grams of the barium salt (Analysis V.).

The results of the analyses are as follows:

	Calculated for $K_2Ba(NO_3)_4$	Found. I.	II.	III.	IV.	V.
K	16.87	17.07	....	16.52	....	....
Ba	29.64	29.69	29.21	29.22	30.45	30.49
NO_3	53.49	52.95	....	52.62	....	....
H_2O	....	....	....	1.89	....	....

In regard to the analyses, it may be mentioned that barium and potassium were weighed as sulphates while nitrogen was determined by the modified Kjeldahl-Gunning method.[1]

The crystals formed by cooling were in white, opaque masses of microscopic individuals, which showed tetrahedral habit, while the crystals obtained by slow evaporation were very much larger, usually from 1 to 3 mm. in diameter. The latter were also white and opaque and were invariably of tetrahedral form. The faces of these crystals were much striated and very rough and imperfect. Prof. S. L. Penfield has kindly inspected the crystals, and has found that they show strong optical properties, although they are too opaque to give any satisfactory results upon examination. Professor Penfield has also pointed out the general resemblance in habit of these crystals to certain crystals of barium nitrate mentioned by Groth.[2] The view that the crystals are impure barium nitrate must therefore be considered. This does not appear to be possible on account of the constant composition of several crops produced under considerably different conditions, and also on account of the close ratios derived from the analyses, which indicate the presence of 2 atoms of potassium to 1 of barium. It should be mentioned also that when crystallizations were made from solutions containing more barium nitrate than potassium nitrate, or when an attempt was made

[1] Bulletin 46, Revised Edition, U. S. Dept. Agr., p. 17.

[2] Physikal. Krystallog., p. 498.

to recrystallize the double salt, barium nitrate was deposited in crystals of octahedral habit, which were more transparent and were different in appearance from the double salt.

Attempts to prepare a double salt with caesium nitrate and barium nitrate were without success. From a solution containing 25 grams of the caesium salt and 15 grams of the barium salt, the two simple salts crystallized out side by side. A similar result was obtained with potassium nitrate and strontium nitrate, for it was found that these two salts crystallized side by side when 10 grams of the first and 18 grams of the second were present in a solution. It does not appear probable, therefore, that a series of double nitrates analogous to $K_2Ba(NO_3)_4$ can be prepared.

It may be said, in conclusion, that the double salt under consideration is curious, not only as an alkali-metal and barium double nitrate, but because a corresponding compound is not formed by caesium, which shows an eminent tendency to form double salts, and also because it crystallizes in imitation of barium nitrate and forms very crude, opaque crystals. It seems possible that these crystals are formed upon nuclei of barium nitrate and that their structure is pseudomorphic.

NEW HAVEN, CONN., April, 1903.

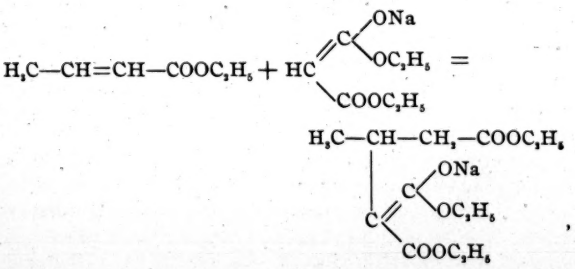
ON THE CONDENSATION OF OXALIC ETHYL ESTER WITH ETHYLENE AND TRIMETHYLENE CYANIDES.

BY ARTHUR MICHAEL.

According to v. Baeyer's strain hypothesis, the facility of the conversion of organic substances with open into those with closed chains is dependent on the spacial proximity of the groups that interact to form the ring. Basing his speculations on the van't Hoff tetrahedron form for the carbon atom, v. Baeyer showed that the strain hypothesis explains the well-known tendency towards the formation of derivatives containing five- or six-membered rings. Although a very

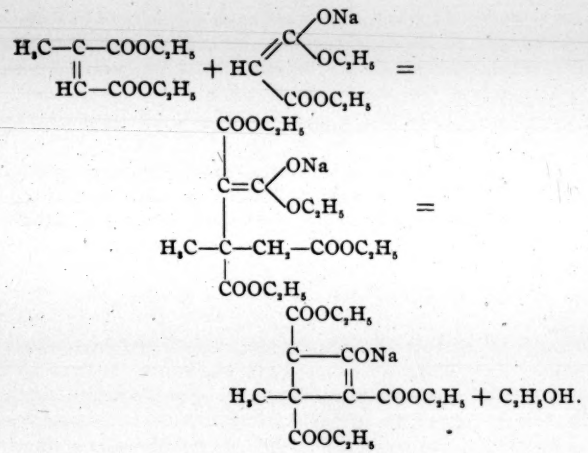
considerable number of facts are in accordance with these views, the strain hypothesis cannot represent a comprehensive explanation for the theory of ring-formation, since it does not take into consideration the question of chemical affinity, nor the influence of side-chains in facilitating such condensations.

That groups, which do not directly enter into the process of forming the ring, may greatly influence the phenomenon has long been known, but until recently the facile condensation of substances with open to those with closed chains invariably implied the formation of derivatives containing a five- or six-membered ring. Indeed, this relationship forms the principal support of the strain hypothesis. Several years ago the writer[1] showed that, through the indirect influence of certain side groups, derivatives of tetramethylene may be obtained not only by alcohol-condensation, but that they are quite as readily formed as any derivatives of five- or six-membered rings. Thus the substance formed by addition of sodium malonic ester to crotonic ester,



is stable, but if β-carbethoxycrotonic ester, *i. e.*, citraconic ester be used, instead of crotonic ester, a very considerable part of the addition-product formed at first undergoes a spontaneous condensation to a derivative of ketotetramethylene:

[1] Ber. d. chem. Ges., 33, 3742.



Furthermore, it was shown that methyl and, to a greater degree, ethyl facilitate these condensations more or less, according to their position towards the malonic-ester radical of the addition-products. This investigation proves conclusively that the strain hypothesis will require material modification before it can offer a satisfactory explanation of the phenomenon of ring-formation, but in this paper it is not proposed to enter more fully on the subject.

In continuing this investigation on the influence of side-chains, some experiments were made to ascertain whether derivatives of tetramethylene could be obtained by means of oxalic ester. The use of succinic ester as second substance for this purpose was debarred, since it readily suffers a chemical change with sodium or sodium ethylate, and succinic nitrile was therefore employed in its place.

The condensation of oxalic ester with benzyl nitrile has been effected by Erlenmeyer, Jr.[1] Subsequently, Fleishhauer[2] extended the reaction, using several fatty nitriles. In the later

[1] Ber. d. chem. Ges., 22, 1483.
[2] J. prakt. Chem., [2], 47, 375.

experiments only poor yields were obtained, but in syntheses like the above it is characteristic of the indirect influence of negative, polyvalent atoms in the fourth position towards the carbon of a methylene group, to greatly facilitate the reactivity of hydrogen joined to such carbon,[1] and since ethylene cyanide fulfils these conditions, more favorable results were expected than when monobasic nitriles are used. The condensation between oxalic ester and ethylene nitrile, using either sodium ethylate or sodium, proceeds readily and a fair yield of a keto-product is formed. The reaction, however, does not lead to a product with a closed chain, but proceeds as follows:

$$2\,\begin{vmatrix} COOC_2H_5 \\ COOC_2H_5 \end{vmatrix} + \begin{vmatrix} CH_2CN \\ CH_2CN \end{vmatrix} = \begin{matrix} H_5C_2OOC-CO-CH-CN \\ \quad\quad\quad\quad\quad\quad\quad\quad | \\ H_5C_2OOC-CO-CH-CN \end{matrix} + 2C_2H_5OH.$$

Since Dieckmann[2] has shown that ketopentamethylene derivatives may be easily synthesized by condensing oxalic ester with glutaric ester, it was expected that using trimethylene cyanide, instead of the ethylene derivative, an analogous product would be obtained. It was found, however, that condensation stops at the first stage of the reaction and attempts to close the chain were without result. The reaction is represented by:

$$\begin{vmatrix} COOC_2H_5 \\ COOC_2H_5 \end{vmatrix} + \begin{matrix} CH_2-CN \\ | \\ CH_2 \\ | \\ CH_2CN \end{matrix} = \begin{matrix} CH_2-CN \\ | \\ CH_2 \\ | \\ H_5C_2OOC-CO-CH-CN \end{matrix} + C_2H_5OH.$$

Action of Oxalic Ester on Ethylene Cyanide.

Five grams of ethylene cyanide[3] were dissolved in 9 grams

[1] Michael: Ber. d. chem. Ges., 33, 3733.
[2] Ann. Chem. (Liebig), 317, 27.

oxalic ethyl ester (equal mols.), the solution cooled to room temperature, and 1.4 grams sodium wire (1 atom) added. The reaction began soon, but was slow, and after the mixture had stood a day there was still a little unchanged sodium. It was finally completed by warming the mixture to about 45° for a short time. Only a small amount of gas was given off. The product, which was a canary-yellow substance suspended in a thick oil, was dissolved with cold water and filtered from a slight residue. Carbon dioxide, passed through the filtrate, gave no precipitate, but addition of hydrochloric acid gave a thick oil. On standing for a day in the ice-chest, this oil solidified to a considerable extent to long, yellowish prisms, which were filtered off under pressure and washed with a little dilute alcohol. For analysis, the dried product was taken up with hot benzene, filtered from a small amount of insoluble, resinous substance, and recrystallized twice from the same solvent.

I. 0.1314 gram substance, dried at 100° *in vacuo*, gave 0.2473 gram CO_2 and 0.0556 gram H_2O.

II. 0.1533 gram substance, dried at 100° *in vacuo*, gave 0.2878 gram CO_2 and 0.0653 gram H_2O.

III. 0.3075 gram substance, dried at 100° *in vacuo*, gave 29 cc. N at 22° and 757 mm.

	Calculated for $C_{12}H_{12}O_6N_2$.	Found. I.	II.	III.
C	51.4	51.3	51.2	...
H	4.3	4.7	4.7	...
N	10.0	...	...	10.6

β,γ-Dicyano-α,δ-diketoadipic ethyl ester crystallizes from alcohol as long, straw-colored prisms, with obliquely truncated ends, which often form fan-shaped groups. It melts under boiling water, but is only sparingly soluble in it. In alcohol it dissolves readily in the cold, also in hot benzene, separating from the latter solvent, on cooling, as small, prismatic needles, which melt at 121° to 123°. Hot petroleum ether dissolves the substance but slightly. Boiled with dilute hydrochloric acid, it is easily saponified, giving a thick oil, which was not further examined. The ester gives the hydrazone reaction with phenylhydrazine acetate. The substance may be obtained by

using alcoholic sodium ethylate instead of sodium. To a cold solution of 1.6 grams sodium (2 atoms) in 20 grams absolute alcohol, 10.8 grams oxalic ester and 3 grams ethylene cyanide (1 mol.) were added. A precipitate began to form in a short time, which increased on allowing the mixture to stand. After addition of some absolute alcohol to this product it was filtered under pressure, washed with alcohol, and dried on a porous plate. This substance forms canary-yellow prisms that are insoluble in hot benzene, acetic ester, and chloroform, and melt at 92° to 96°. In warm absolute alcohol it dissolved readily, but it underwent a change, as the precipitate deposited from the solution on cooling was now not soluble in warm alcohol. The yellow substance contained sodium, and the addition of a mineral acid to its solution in cold water gave a precipitate which, after recrystallization from benzene, melted at 121° to 123° and was identical with the condensation-product obtained by using sodium. It was apparently the sodium derivative of the dicyanoketoadipic ester.

Action of Oxalic Ethyl Ester on Trimethylene Cyanide.

In preparing trimethylene cyanide, according to the directions given by Henry,[1] a potassium cyanide was employed that was supposed to be a 98 to 99 per cent pure product. On fractionating the product of the reaction, some oil was obtained that boiled considerably lower than trimethylene cyanide, and after several fractionations with beads in vacuum, 5 grams (from 137 grams trimethylene bromide) of an oil, boiling constantly at 91° C. under 12 mm. pressure, were isolated. The product contained bromine and, as the following halogen estimation showed, was formed by the replacement of one bromine in trimethylene bromine by the cyanogen radical:

0.2052 gram oil gave 0.2597 gram AgBr.

	Calculated for $CH_2Br—CH_2—CH_2—CN$.	Found.
Br	54.2	53.8

The formation of this substance is analogous to that of trimethylene chlorocyanide from trimethylene chlorobromide and

[1] Compt. rend., 100, 742.

potassium cyanide. Its appearance was probably due to the use of potassium cyanide, which was less pure than was supposed, since a subsequent preparation of the cyanide, when pure potassium cyanide was employed, gave only trimethylene cyanide.

To a solution of 5 grams trimethylene cyanide in 7.8 grams oxalic ethyl ester (equal mols.) 1.25 grams sodium wire (1 atom) were added and, as the metal did not react in the cold, the mixture was heated to 40°, when the reaction began. The flask was then removed from the water-bath and in about an hour, at room temperature, almost all the metal was used up. The few remaining shreds of sodium disappeared on warming the flask gently for an hour. The brown product was taken up with cold water and carbon dioxide passed through the solution as long as a precipitate was formed. This precipitate was inconsiderable and was not examined. The addition of hydrochloric acid to the filtrate from this precipitate gave an oil that soon solidified to a mass (4 grams) of large crystals. For analysis the substance was treated in benzene solution with bone-black, and recrystallized twice from that solvent and then once from hot water.

0.1359 gram substance gave 0.2773 gram CO_2 and 0.0678 gram H_2O.

0.3700 gram substance gave 49 cc. N at 21° and 754.6 mm.

	Calculated for $C_9H_{10}O_5N_2$.	Found.
C	55.7	55.6
H	5.1	5.5
N	14.4	14.8

β,δ-Dicyano-α-ketoglutaric ester crystallizes from benzene as almost white, six-sided prisms, generally with truncated ends, that melt at 96° to 98°. It is but slightly soluble in cold water and benzene; readily in these solvents when hot; and sparingly soluble in ligroin, ether, and carbon tetrachloride. In dilute alkalies it dissolves and is precipitated unchanged by addition of a mineral acid to the solution. The ester gives with phenylhydrazine acetate the hydrazone reaction for the presence of a keto group. Boiled with dilute hydrochloric

acid it was easily saponified, with evolution of carbon dioxide, and a thick, oily acid was formed, which could not be obtained in a solid state.

The substance was also prepared by using alcoholic sodium ethylate. One gram sodium (1 atom) was dissolved in 12 grams absolute alcohol, the solution cooled, 6 grams oxalic ester (1 mol.) and then 4 grams trimethylene cyanide (1 mol.) added. The mixture was placed a day in the ice-chest and then allowed to stand for several days at the temperature of the room. A crystalline precipitate formed, which was filtered, washed with alcohol, and then dissolved in water. Addition of hydrochloric acid to the aqueous solution gave 3.9 grams of the substance in an almost pure state.

Several experiments were made to obtain a cyclopentene derivative from oxalic ester and trimethylene cyanide. The experiment just described was repeated with the variation of using 2 molecules of sodium ethylate to 1 molecule of cyanide. The solution became dark-red after standing several days, but no precipitate was formed. After evaporation of the alcohol in vacuum, the residue was dissolved in water and a slight excess of hydrochloric acid added to the solution. The copious precipitate was not a pure substance, it melting partially at 78° to 80° and at 175° to 185°, and left a mineral residue on calcination. Extracted with hot benzene, about two-thirds dissolved, and the above-described keto ester separated from the solution on cooling. Equally unsuccessful was an experiment using 2 atoms sodium to 1 molecule of the cyanide, and also the action of sodium ethylate on the dicyanoketoglutaric ester.

A number of experiments were made to obtain condensation-products of ethylene and trimethylene cyanides with mono- and diethyl malonic and glutaric esters, using sodium for the purpose. The metal did not act readily on these mixtures and heat was required to use it up. In no case was more than a small yield of an acidic oil obtained.

TUFTS COLLEGE, MASS.

REVIEWS.

THE STORY OF ALCHEMY AND BEGINNERS OF CHEMISTRY. By M. M. PATTISON-MUIR. New York: D. Appleton & Co. 1903. pp. 185.

In the last fifteen years Berthelot has minutely described in six folio volumes the beginning of alchemy in Egypt and shows how the art, surviving the destruction of the Alexandrian library and the Roman eviction of the alchemists from Egypt, wandered degraded through Chaldea and Mesopotamia to Constantinople and how finally, reaching Europe in the thirteenth century, misunderstood even by its promoters, it took the same disgraceful rank as astrology and magic.

It is surprising, at this late day, to find Mr. Muir describing the alchemy of the sixteenth century as alchemy *par excellence*, and so condemning it as unintelligible and comparing the tottering structure with the philosophical systems of the Greeks. Two facts need to be held in mind to give us a clear view of this subject. First, alchemy was an art—it was neither a philosophical or theological system; second, it was, as an art or handicraft, Egyptian, and its literature and language, even in the sixteenth century, may be made surprisingly intelligible by reflecting upon it the Egyptian conception of nature.

The later alchemy may contain "A language that is inexact, undescriptive, and unsuggestive to modern ears," and yet we are not justified in speaking, as does Mr. Muir on his opening page, of "One very curious manufacture wherein not the thousandth fragment of a grain of the finished article was ever produced." No portion of what we now understand as gold was ever produced, yet, what the Egyptian meant by gold was produced abundantly, for, in Egypt, "gold" meant often a purple bronze or iridescence. (*Chemical News*, 85, 49.)

The author's general attitude towards alchemy, as he interprets it, is condemnatory. So far as page 122 he describes the bombast and fairy tales of the period as though they were essential parts of a system. Chapter VI., however, contains a very good description of "Alchemy as an experimental art," fully illustrated by cuts. The errors of the work may perhaps be answered curiously enough by Mr. Muir's own words: "It would be truly absurd to carry back to that time the meaning that we give to these terms to-day and then to brand as ridiculous the attempts of the men who studied then the same problems that we study now."

The last third of the book is devoted to a masterly description of the transition from alchemy to the chemistry of Lavoisier. Here the author is strong and the theme is well sus-

tained to the end. The book is small, with flexible covers. It is published in an attractive form as one of "The Library of Useful Stories," and, taken as a whole, is a delightful book to read. A. J. H.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. II. BAND. DIE GEWINNUNG DES ALUMINIUMS, UND DESSEN BEDEUTUNG FÜR HANDEL UND INDUSTRIE. Von ADOLPHE MINET. Ins Deutsche übertragen von DR. EMIL ABEL. Wien: Wilhelm Knapp. Halle, a. S. 1902.

As the title implies, the monograph discusses the various methods by which the element aluminium is obtained. The methods are divided into two general classes—chemical and electrochemical. The former include the reduction of aluminium compounds by sodium and other substances, and the latter the various electrical processes which have been employed in obtaining aluminium.

The work in hand contains a discussion of much of the same material included by Borchers in his "Elektrometallurgie." The second part of this monograph takes up such questions as the cost of producing aluminium, the alloys of aluminium, and the aluminium industry in general. H. C. J.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. III. BAND. DIE DARSTELLUNG DES CHROMS UND SEINER VERBINDUNGEN, MIT HILFE DES ELEKTRISCHEN STROMES. Von DR. MAX LA BLANCORD, Professor und Direktor des Physikalisch-chemischen (Elektrochemischen) Instituts der Technischen Hochschule zu Karlsruhe. Halle, a. S. Wilhelm Knapp. 1902.

This monograph on the preparation of chromium and its compounds gives a review of the electrical methods used for that purpose up to the end of the year 1901. The methods are classified under the general heads: Preparation of metallic chromium by electrolysis from aqueous solution, and at high temperatures; preparation of compounds of chromium with metals by electrolysis from aqueous solution, and at high temperatures; and preparation of the compounds of chromium with the non-metals, such as carbon, silicon, phosphorus, sulphur, oxygen, etc.

The work is written with that unusual clearness which is characteristic of its author. H. C. J.

PHYSICAL CHEMISTRY FOR PHYSICIANS AND BIOLOGISTS. By DR. ERNST COHEN, Professor of General and Inorganic Chemistry in the University of Utrecht. Authorized translation from the German, by MARTIN H. FISCHER, M.D., Instructor in Physiology in the University of California. New York: Henry Holt & Co. 1903. pp. 343.

The work in hand was prepared, according to the author,

"in response to the request of a number of physicians to give in a series of lectures a résumé of those subjects in physical or general chemistry which are of importance in medicine. These lectures are in no way a text-book of physical chemistry. I have merely endeavored to show in them the close relation that exists between this new branch of chemistry and the biological sciences." The lectures are on reaction velocity, inversion of cane-sugar and catalysis in general, the action of ferments, temperature and reaction velocity, equilibrium, friction of liquids, osmotic pressure, molecular weight of dissolved substances, the theory of electrolytic dissociation, applications. The importance of physical chemistry in connection with the biological sciences is becoming greater and greater, and there is a growing demand on the part of biologists to know more and more of the recent developments in physical chemistry. The book under consideration will undoubtedly prove useful in the field which it is meant to cover. A question which may fairly be raised is whether the average physician is sufficiently familiar with the calculus and differential equations to use successfully a work into which they are extensively introduced. The work is clearly written, and the English translation seems to be satisfactory. H. C. J.

INORGANIC CHEMISTRY SYLLABUS. By HUBERT C. CAREL, B.S., Assistant Professor in the University of Minnesota. Third Edition. Minneapolis: H. W. Wilson. 1902.

The author's preface says that "this little book is an effort to present in brief form, those salient facts of inorganic chemistry as offered to the Freshman classes of the Department of Medicine, University of Minnesota. The chief object has been brevity, to which we have sacrificed everything save accuracy and definition." The writer has been successful, for the book contains a surprising amount of condensed descriptive chemistry. Indeed, there is almost too much detail for a book in which the single subjects are treated so briefly, and there would be danger of the student not grasping the relative value of the facts presented, were the book used alone, but used as it is with lectures and laboratory, it is doubtless of value. E. R.